Water-Soluble Polymers from Controlled Free-Radical Polymerisation

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A CONTENTS

Section B TABLE OF FIGURES

Section C TABLE OF TABLES

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E DECLARATION

All experimental work contained in this thesis is original research that was carried out by the author in the Department of Chemistry, University of Warwick or at Unilever Research, Port Sunlight, between October 1996 and October 1999. No material contained herein has been submitted for any other degree to this, or any other, institution. Results from other authors are referenced in the usual manner throughout the text.

Signed 

Date 9-6-2000

F SUMMARY

Functional water-soluble polymers are used in the detergents industry as anti-dye transfer agents. Anti-dye transfer agents are materials that complex with dye in solution and therefore prevent the transfer of dye between clothing during the laundering cycle. Current commercially available anti-dye transfer agents are based on homopolymers or statistical co-polymers that contain poly(N-vinyl pyrrolidone). These polymers are covered by extensive patent protection from various companies and have also been shown to precipitate from solution at high dye concentrations. Novel free-radical polymerisation techniques have been used here to prepare controlled architecture polymers based on poly-2-(dimethylamino)ethyl methacrylate that contain hydrophilic, anionic and cationic functionality. Free-radical polymerisation has been used to prepare statistical co-polymer species that contain quaternary charge. Atom transfer polymerisation (ATP) has been used to prepare gradient co-polymers and catalytic chain transfer polymerisation has been used to prepare macromonomers as precursors to block co-polymer products.

The dye-binding constants of these novel polymers have been determined using an adaptation of the static sorption technique with Direct Red 80 azo-dye in deionised water and in anionic surfactant stock solution. The data from these tests have improved reproducibility compared with previous studies and tests containing anionic surfactant have highlighted the shortcomings of the static sorption model previously used to determine the dye-binding ability of polymers with dye in deionised water.

Hydrophilic gradient co-polymers that contain one dye-binding functionality and one water soluble functionality have been found to offer no significant increase in the dye-binding ability of the polymer species in comparison with the equivalent statistical co-polymer species.

G ABBREVIATIONS

AA	Acrylic acid
ADMIBA.HCl	2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride
AIBN	2,2'-azobisoobutyronitrile
ATP	Atom transfer polymerisation
ATRA	Atom transfer radical addition
Bpy	2,2'-bipyridine
BzA	Benzyl acrylate
BzMA	Benzyl methacrylate
CCT	Catalytic chain-transfer
CCTA	Catalytic chain-transfer agent
CCTP	Catalytic chain-transfer polymerisation
CoBF	[Bis[μ-[(2,3-butanedione dioximato)(2-)-O:O']]tetraflurodiborato(2-)-N,N',N'',N'''] cobalt
Cs	Chain transfer co-efficient
CVA	4,4'-azobis(4-cyanovaleric acid)
DMAEIB	2-(dimethylamino)ethyl isobutyrate
DEAEMA	2-(diethylamino)ethyl methacrylate
DMAEMA	2-(dimethylamino)ethyl methacrylate
DMAEMA.HCl	2-(dimethylamino)ethyl methacrylate, hydrochloride salt
DMAEMA.MeI	[2-(methacryloyloxy)ethyl]trimethylammonium iodide
Dp	Degree of Polymerisation
GPC	Gel permeation chromatography
HMTETA	1,1,4,7,10,10-hexamethyltriethylenetetramine
IR	Infra-red
K_P	Dye binding constant for a water soluble polymer
K_S	Dye binding constant for a water insoluble polymer
MAA	Methacrylic acid
MeI	Methyl iodide
MMA	Methyl methacrylate
Mn	Number average molecular weight

Mw	Weight average molecular weight
NMR	Nuclear magnetic resonance
PDi	Polydispersity Index
ppm	Parts per million
PBzMA	Poly(benzyl methacrylate)
PDEAEMA	Poly[2-(diethylamino)ethyl methacrylate]
PDMAEMA	Poly[2-(dimethylamino)ethyl methacrylate]
PMAA	Poly(methacrylic acid)
PMMA	Poly(methyl methacrylate)
1,3-PS	1,3-propane sultone
PVCap	Poly(N-vinylcaprolactam)
PVI	Poly(vinylimidazole)
PVP	Poly(N-vinyl-2-pyrrolidone)
PVPip	Poly(N-vinylpiperidone)
PVPy-NO	Poly(N-vinylpyridine-N-oxide)
RAFT	Reversible addition-fragmentation transfer
SFRP	Stable free-radical polymerisation
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
TEMP-Sty	2,2,6,6-tetramethyl-1-(1-phenylethoxypiperidine)
THF	Tetrahydrofuran
UV	Ultra-violet

Chapter 1

INTRODUCTION

A problem is a chance for you to do your best.

Duke Ellington

1.0 INTRODUCTION

Recent developments in free-radical polymer synthesis have allowed for a greater degree of control over the molecular weight distribution, architecture and functionality to be achieved [1]. These novel polymerisation techniques have provided routes for the synthesis of new low cost polymers from currently commercially available monomers. One area that has experienced rapid growth is research into the development of novel, multifunctional and architecturally controlled water-soluble polymers [2,3]. Water-soluble polymers have found widespread use in special applications including drug delivery systems [4] and biotechnology [5] as well as in the high volume market, such as additives for household products [6,7]. This study has investigated the synthesis and solution properties of a series of novel water-soluble polymers for use in the detergents industry as Anti-Dye Transfer Agents from controlled radical polymerisation techniques. This introduction will review the basic theory of polymer science and will provide a general overview of the areas of controlled radical polymerisation and water-soluble polymers.

1.1 POLYMER CHEMISTRY

A polymer is a high molar mass molecule that consists of a large number of low mass repeat units that are connected by covalent bonds. If a polymer consists only of a single type of repeat unit then it is said to be a homopolymer and can be represented by Figure 1.0.

Figure 1.0 Homopolymer of A

~A-A-A-A-A-A~ or $-[A]-_n$

A is a base unit and n is the degree of polymerisation, DP or chain length.

Base units are not individual molecules but are polymerised forms of their molecular equivalents known as monomers.

Figure 1.1 Polymerisation of Monomer to produce Base Unit

Monomer	Base Unit
$CHCl=CH_2$	$-[CHClCH_2]-$
vinyl chloride	polyvinyl chloride

1.1.1 Polymer Conformation and Architecture

Composition and architecture both play important roles in the physical properties of polymers, providing control over solubility, thermal behaviour, viscosity and compatibility. Base units may be assembled in several different chain conformations. Figure 1.2 outlines the principal types of chain assembly found in polymeric materials.

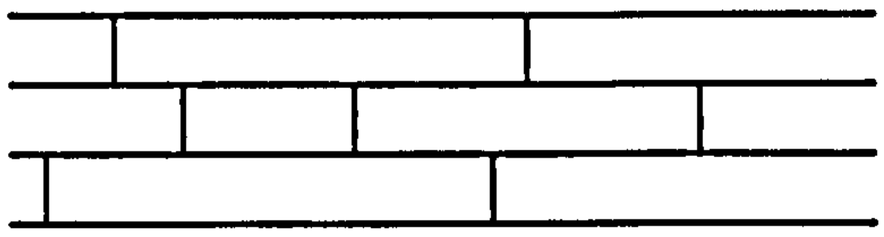
Figure 1.2 Classification by Chain Structure

Linear polymers: ~A-A-A-A-A-A~

Branched polymers:

~A-A-A*-A~
|
A-A-A-A*-A~
|
A-A-A~

Network polymers:



Polymers that are formed from two or more different types of monomer can have several different microstructures. Figure 1.3 illustrates some of the types of

monomer composition available with up to three different monomeric species present.

Figure 1.3 Classification by Monomer Composition

Homopolymers: ~A-A-A-A-A-A-A-A-A~ or $-[A]_n-$

Statistical Co-polymers: ~A-A-B-A-B-B-A-A-B~

Alternating Co-polymers: ~A-B-A-B-A-B-A-B-A~ or $-[A-B]_{n/2}-$

Block Co-polymers: ~A-A-A-A-A-B-B-B-B~ or $-[A]_n-[B]_m-$

Graft Co-polymers:

```
~A-A-A-A*-A-A-A-A-A~
          |
          B-B-B-B-B~
```

Random Terpolymers: ~A-A-B-C-A-C-B-B-C-A-A~

1.1.2 Molecular Weight Distribution

A truly monodisperse polymer exists as single discrete molecule of only one molecular mass and conformation, some natural polymers are of this type. Synthetic polymers are said to be polydisperse. Polydisperse polymers exist in a state where the degree of polymerisation, n, covers a range of values. The distribution of the number of each species with a certain degree of polymerisation varies depending on the polymer. The molecular weight distribution of a polymer is an important factor in determining the physical characteristics of the polymer species and therefore the analysis and control of this distribution has attracted considerable interest. Several mathematical relationships have been defined to represent this distribution [8].

1.1.2.1 Number Average Molecular Weight, M_n

The number average molecular weight of a polymer, M_n is an evaluation of the number of species in the polymer of each weight. The sum of the weights of each species will be equal to the total weight of the polymer, w. N_i and M_i. are the number and the molecular weight of each species respectively. M_n is defined by the following equation as

$$\overline{M}_n = \frac{w}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i} \qquad (1.0)$$

1.1.2.2 Weight Average Molecular Weight, M_w

The weight average molecular weight of a polymer, M_w is a measure of the weight fraction of each species present in the sample.

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} w_i M_i}{\sum_{i=1}^{\infty} w_i} = \frac{\sum_{i=1}^{\infty} M_i^2 N_i}{\sum_{i=1}^{\infty} N_i M_i} \qquad (1.1)$$

1.1.2.3 Polydispersity Index, PDi

For synthetic polymers the magnitude of M_w when compared with that of M_n is always greater due to a distribution in the molecular weights occurring. The breadth of this distribution is given as a quantitative measurement, the heterogeneity index or polydispersity index (*PDi*) of the sample.

$$PDi = \frac{M_w}{M_n} \qquad (1.2)$$

For monodisperse samples such as proteins where $M_n = M_w$ the $PDi = 1$. For synthetic polymer species $PDi > 1$. The type of mechanism involved in the polymer synthesis can influence the molecular weight distribution in a polymer sample. Synthetic polymers that have a $1.0 < PDi < 1.3$ are generally referred to as near monodisperse.

1.2 ANTI-DYE TRANSFER ACTIVITY

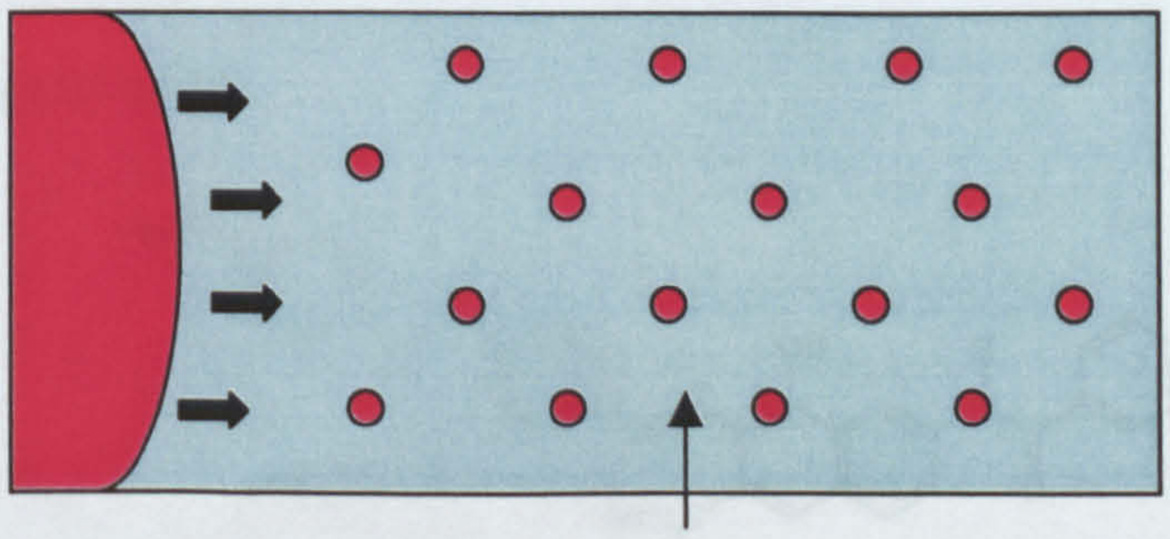
One of the most challenging areas of scientific interest in the detergents industry is the prevention of dye-transfer during the laundering process. During laundering certain dyes can be transferred from coloured to white fabrics resulting in undesirable colour changes and staining. In simple terms this process can be broken down into three steps (Figure 1.4).

Figure 1.4 Dye Transfer

1) Dye is in a bound state, attached to the fabric surface prior to laundering.

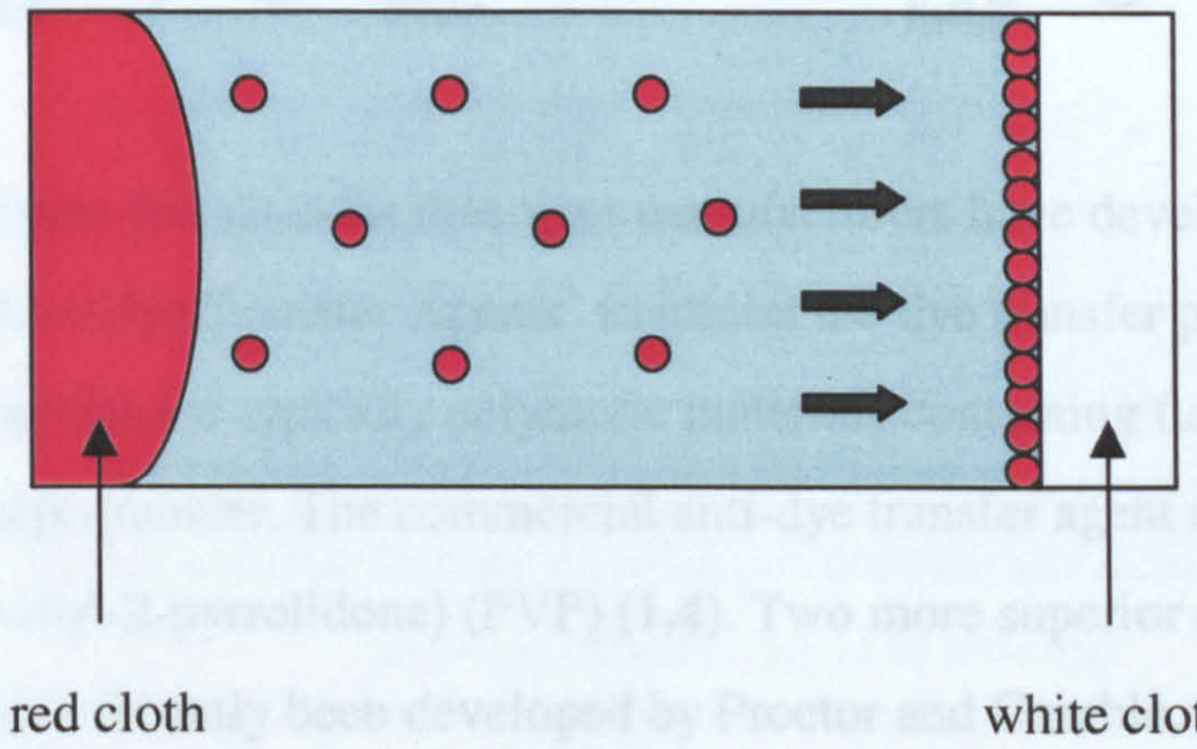
dyed red cloth

2) During the wash process some dye is released from the fabric as free-dye and is distributed into the wash solution.



free-dye in solution

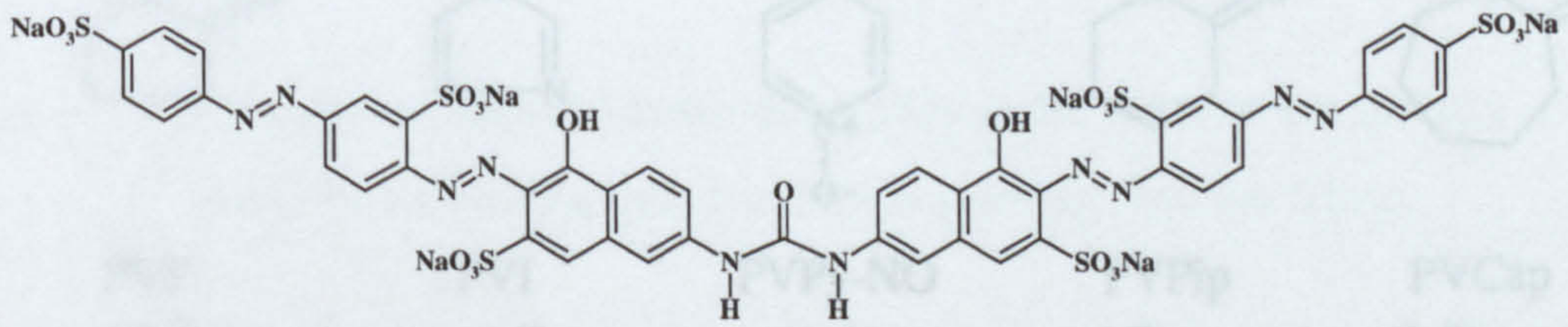
3) Free-dye can deposit onto fabric in the wash resulting in dye transfer between clothing.



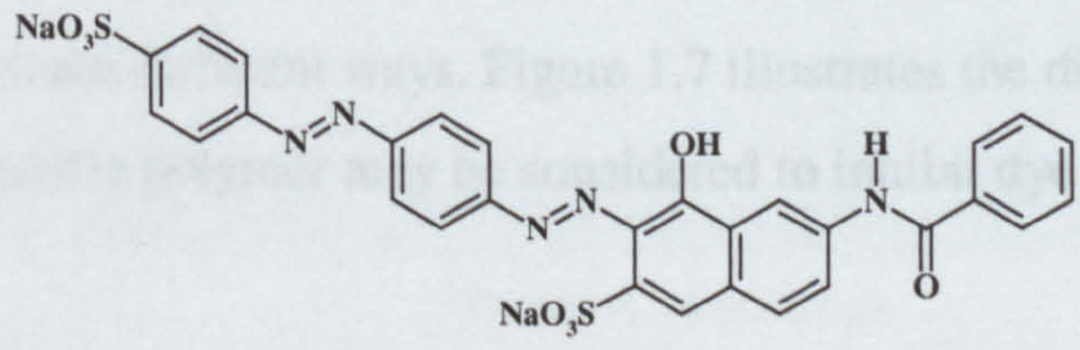
Typical dyes that are used by the fabric industry are anionic azo-dyes. These dyes are rigid aromatic compounds, typically containing anionic groups such as sulfonates or carboxylates. Figure 1.5 illustrates three commercial examples of these dye types.

Figure 1.5 Commercial Azo-dyes

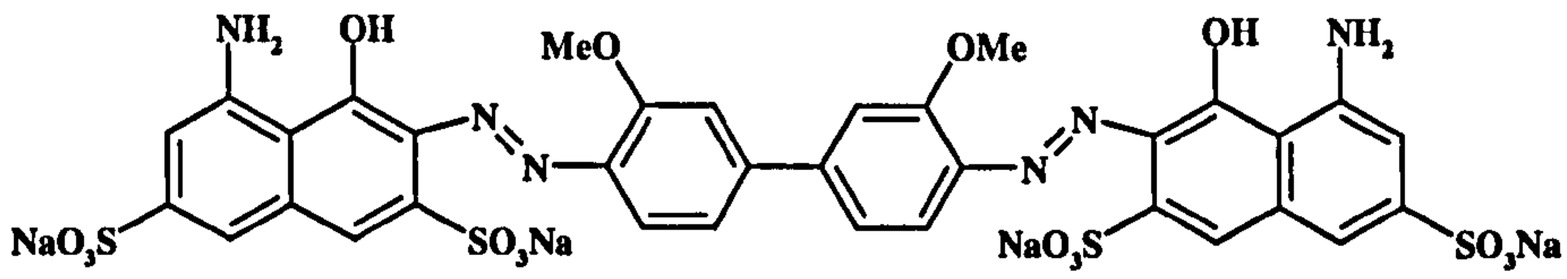
Direct Red 80 (**1.1**)



Direct Red 81 (**1.2**)

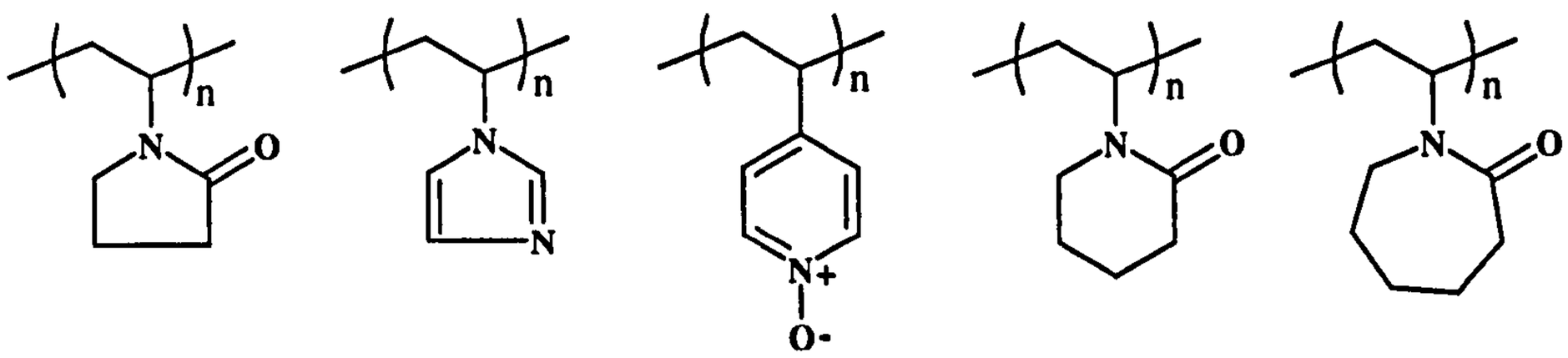


Direct Blue 15 (**1.3**)



Over the past few decades detergent manufacturers have developed and used so called 'Anti-Dye Transfer Agents' to inhibit the dye transfer process. Anti-dye transfer agents are typically polymeric materials containing functionality that inhibits dye-transfer. The commercial anti-dye transfer agent of choice is poly(N-vinyl-2-pyrrolidone) (PVP) (**1.4**). Two more superior anti-dye transfer agents have recently been developed by Proctor and Gamble, these are poly(N-vinylimidazole) (PVI) (**1.5**) [9] and poly(4-vinylpyridine N-oxide) (PVPy-NO) (**1.6**) [10]. Other homologues of poly(N-vinyl-2-pyrrolidone) are also recognised as anti-dye transfer agents, these include poly(N-vinylpiperidone) (PVPip) (**1.7**) and poly(N-vinylcaprolactam) (PVCap) (**1.8**). Figure 1.6 illustrates several examples of known anti-dye transfer agents.

Figure 1.6 Commercially available Anti-Dye Transfer Agents

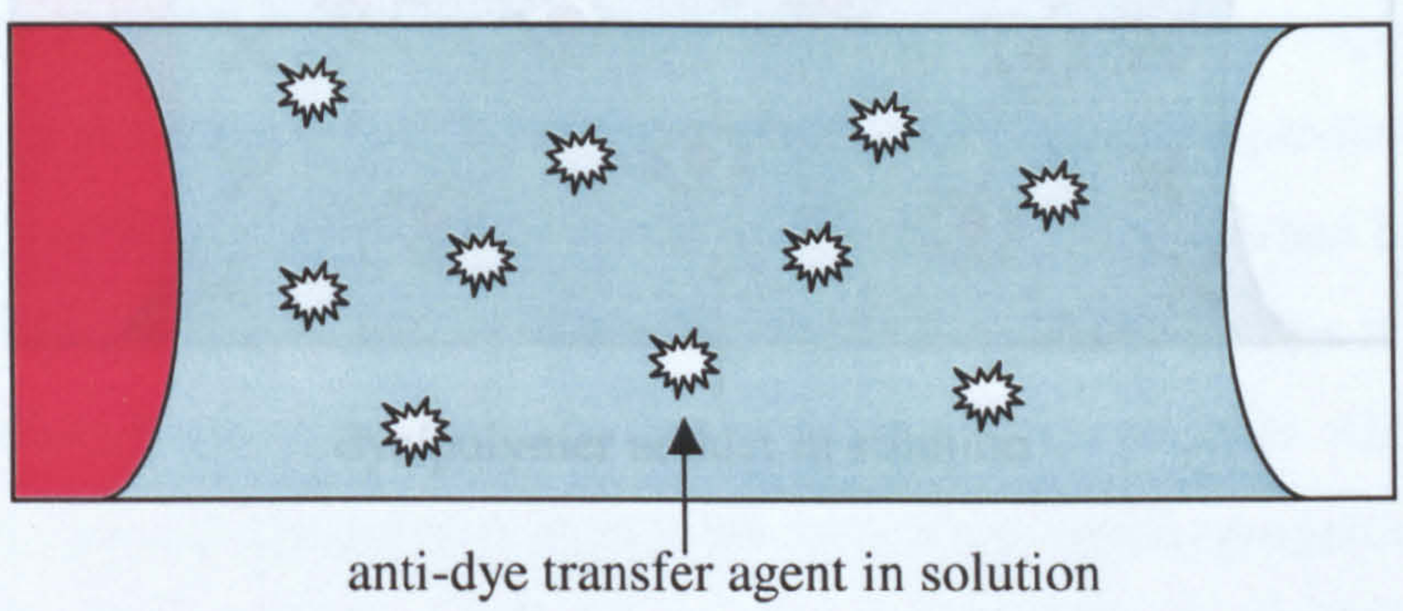


PVP (**1.4**) PVI (**1.5**) PVPy-NO (**1.6**) PVPip (**1.7**) PVCap (**1.8**)

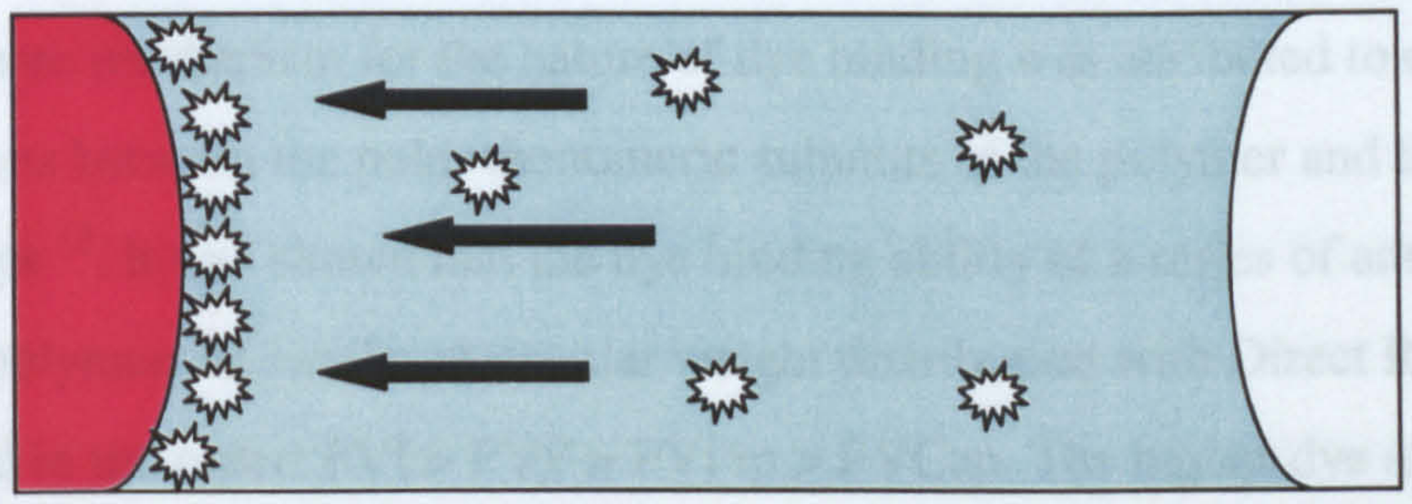
The mechanism through which anti-dye transfer activity occurs may be considered in three different ways. Figure 1.7 illustrates the different ways that an anti-dye transfer polymer may be considered to inhibit dye transfer during laundering.

Figure 1.7 Anti-Dye Transfer Activity

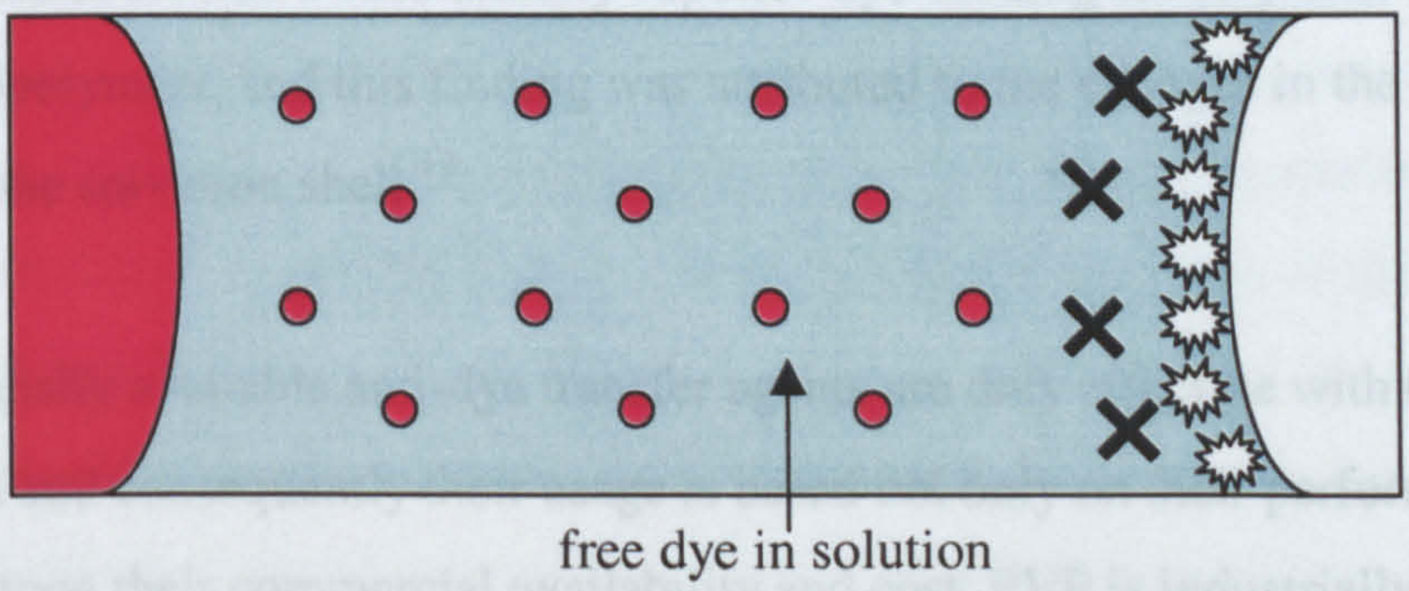
A red dyed cotton cloth and a white non-dyed cotton cloth are placed into an aqueous solution containing an anti-dye transfer agent.



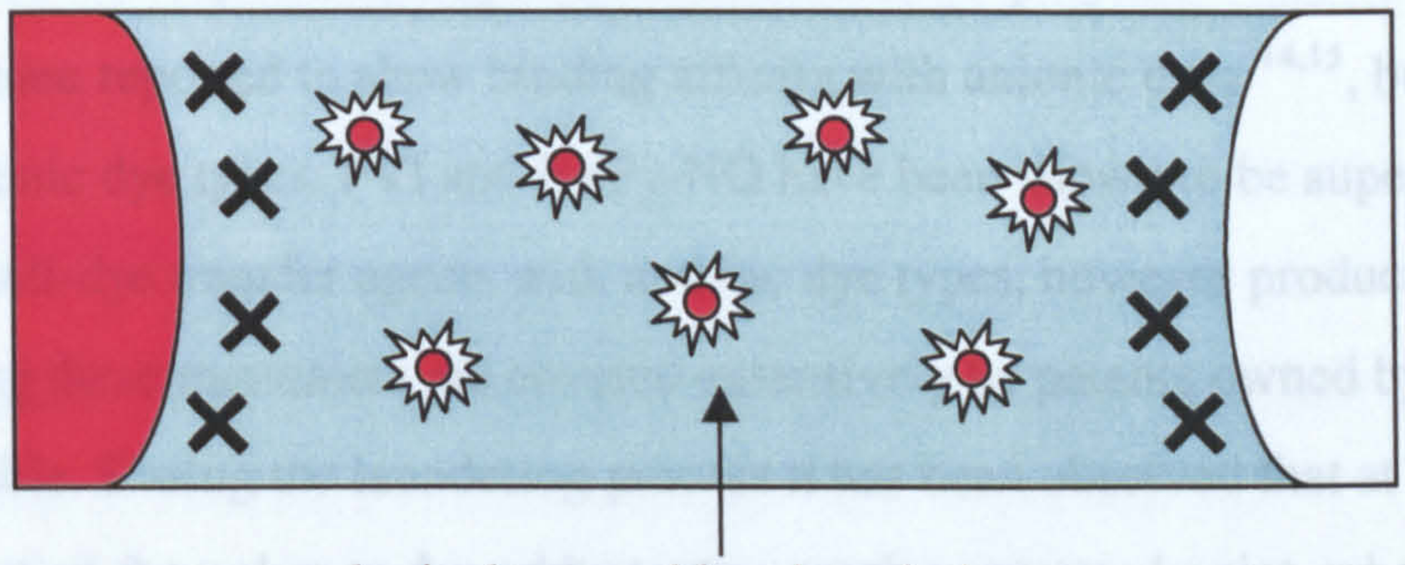
1) The polymeric anti-dye transfer agent binds at the dyed fabric surface, behaving as a fixing agent by inhibiting dye release into solution.



2) The polymer deposits onto vacant sites at the white fabric surface, therefore preventing free-dye from depositing onto the fabric.



3) The polymer remains in the aqueous solution and binds with free-dye to form polymer/dye adducts which are then unable to re-deposit onto the fabric surface.



Jäger *et al* postulate that the underlying mechanism for the anti-dye transfer process follows path 3, where the formation of water-soluble polymer/dye adducts prevents dye from re-depositing onto fabric [11]. Investigations into the nature of the binding between anti-dye transfer polymers and anionic azo-dyes have been reported in the literature. In a recent study by Runge *et al* the predominate mechanism for the nature of dye binding was attributed to dipolar interactions between the polar monomeric subunits of the polymer and the polar dye groups [12]. It was shown that the dye binding ability of a series of anti-dye transfer polymers of similar molecular weight distribution with Direct Red 81 decreased in the order: PVI > PVP > PVPip > PVCap. The higher dye affinity of PVI compared to PVP is explained in terms of the higher value of the dipole moment of the imidazole group compared to that of the pyrrolidone group. The formation of dye/polymer adducts is also followed by a reorganisation in the extended solvation shell. The random co-polymer of N-vinyl-2-pyrrolidone and N-vinylimidazole had a substantially superior dye-binding affinity than either of the homopolymers, and this finding was attributed to the changes in the size and shape of the solvation shell [12].

Commercially available anti-dye transfer agents are only effective with certain dye types and consequently their usage is based not only on their performance but also upon their commercial availability and cost. PVP is industrially used in a range of personal care products including hair care formulations, where they

provide cohesive styling properties that aid hair management [13]. The high demand for PVP and its related co-polymer species with other important monomer types such as N-vinyl imidazole and vinyl acetate has ensured that PVP is now a cheap and readily available commercial polymer [9,10]. PVP based polymers are reported to show binding affinity with anionic dyes [14,15], but none with cationic dye types. PVI and PVPy-NO have been shown to be superior to PVP as anti-dye transfer agents with anionic dye types, however products containing these monomers are covered extensively by patents owned by Proctor and Gamble. During the laundering process it has been observed that at high dye concentration the polymer-dye adducts may reach a saturated point, where dye molecules bound to the polymer change the adduct's solubility properties and precipitation from aqueous solution may occur. Precipitation during laundering has been observed in many leading 'colour' detergents as a fine white precipitate on the fabric surface after laundering. This precipitation is undesirable and research into the development of alternative anti-dye transfer polymers from alternative monomers with improved aqueous properties is currently of great interest.

The incorporation of a hydrophilic co-monomer functionality into the polymer architecture can be used to improve aqueous solution properties of the adduct species. This project has focused on the development of anti-dye transfer polymers containing monomers with tertiary amine functionality that should impart anti-dye transfer activity and their co-polymer products with hydrophilic co-monomers. A non-quantitative study by Jäger *et al* showed that for PVP co-polymers containing anionic/hydrophilic monomers, such as acrylic acid that the anti-dye transfer activity was reduced compared to that for the PVP homopolymer [11]. The incorporation of anionic/hydrophilic groups into the anti-dye transfer agent destabilises the dye/polymer adduct, thus its formation is suppressed. The functionality and the conformational distribution of the hydrophilic co-monomer into a product co-polymer may influence the relative dye-binding affinity, but to date no studies have been performed to determine this effect. In this body of research anionic and cationic hydrophilic monomers have been co-polymerised with a dye-binding monomer to produce co-polymers

with controlled conformation. The effects of the conformational distribution and hydrophilic functionality have been assessed for their effect on the dye binding affinity. The ability of a water-soluble polymer to bind with dye is quantified by calculating the dye-binding equilibrium constant, K_P.

1.2.1 Dye-Binding Tests

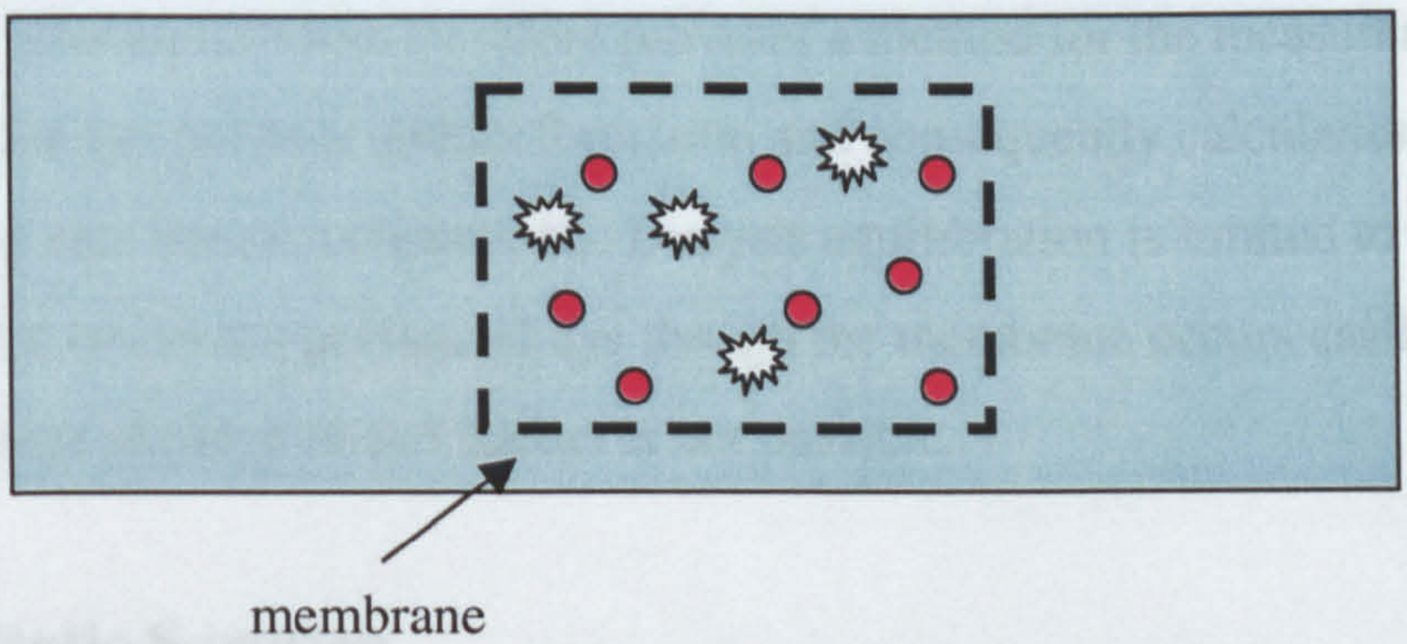
Two quantitative methods are generally accepted for the measurement of the dye-binding equilibrium constant for a water-soluble polymer K_P.

1.2.1.1 Dialysis Equilibration

The mechanism of dialysis equilibration is outlined in figure 1.8.

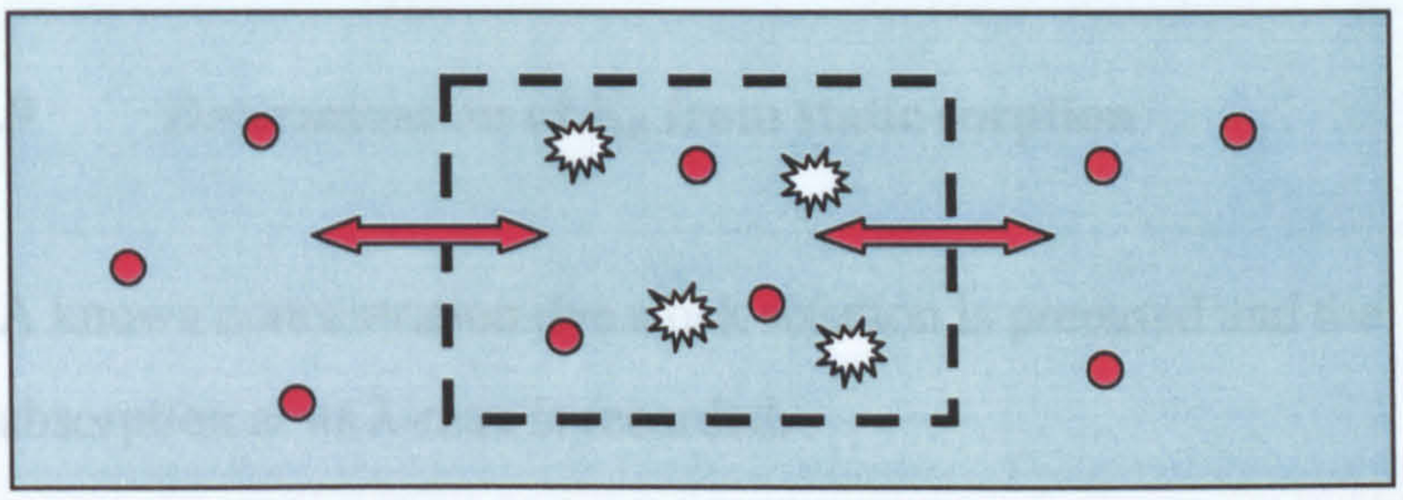
Figure 1.8 Dialysis Equilibration

1) The polymeric anti-dye transfer agent and the dye are placed into an aqueous solution inside a dialysis membrane that allows transfer of the dye across the membrane but which excludes transfer of the polymer.

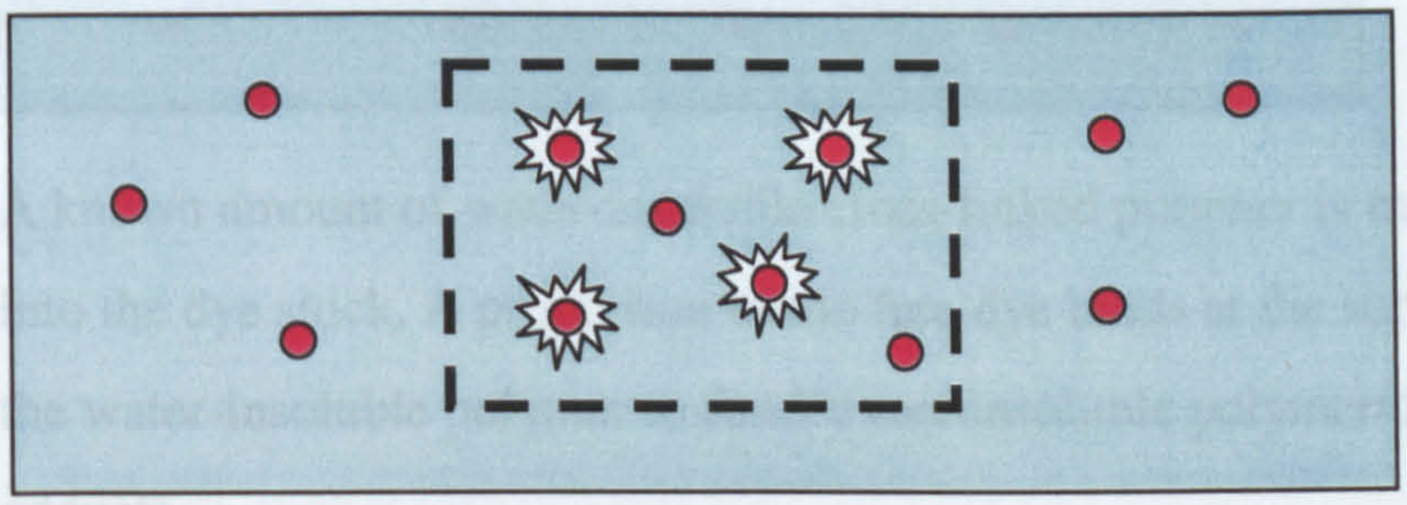


2) The dye is of relatively low molecular weight and has a hydrodynamic volume that can easily pass through the membrane into a void aqueous stock solution. The polymer however is of relatively high molecular weight and has a larger hydrodynamic volume that is excluded from passage through the membrane. When no interaction occurs between

dye and polymer, the passage of the dye across the membrane is facile, allowing equilibrium to be reached where the concentration of dye is the same on both sides of the membrane.



4) The formation of the dye-polymer adduct inside the membrane produces a complex that is incapable of transport across the membrane.



The measurement of the λ max for the free dye that has passed through the membrane after equilibrium therefore provides a method for the measurement of the extent for dye-polymer adduct formation and consequently calculation of the dye-binding equilibrium constant, K_P. Dialysis equilibration is limited to use with systems where the passage of dye though the membrane occurs easily and where passage of polymer and adduct is not possible.

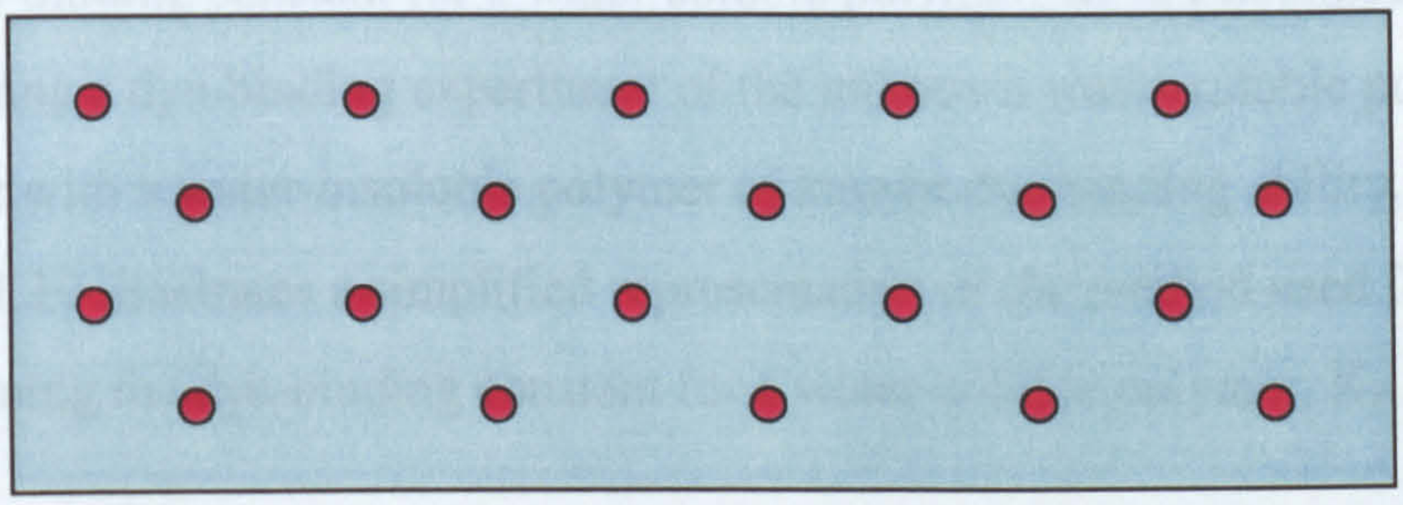
1.2.1.2 Static Sorption

It has been reported that for certain surface-active polymer species an interaction between the polymer and the membrane can induce pore blocking, therefore stopping all transfer across the membrane [12]. Static sorption was developed as an alternative technique for the calculation of K_P for surface-active polymers

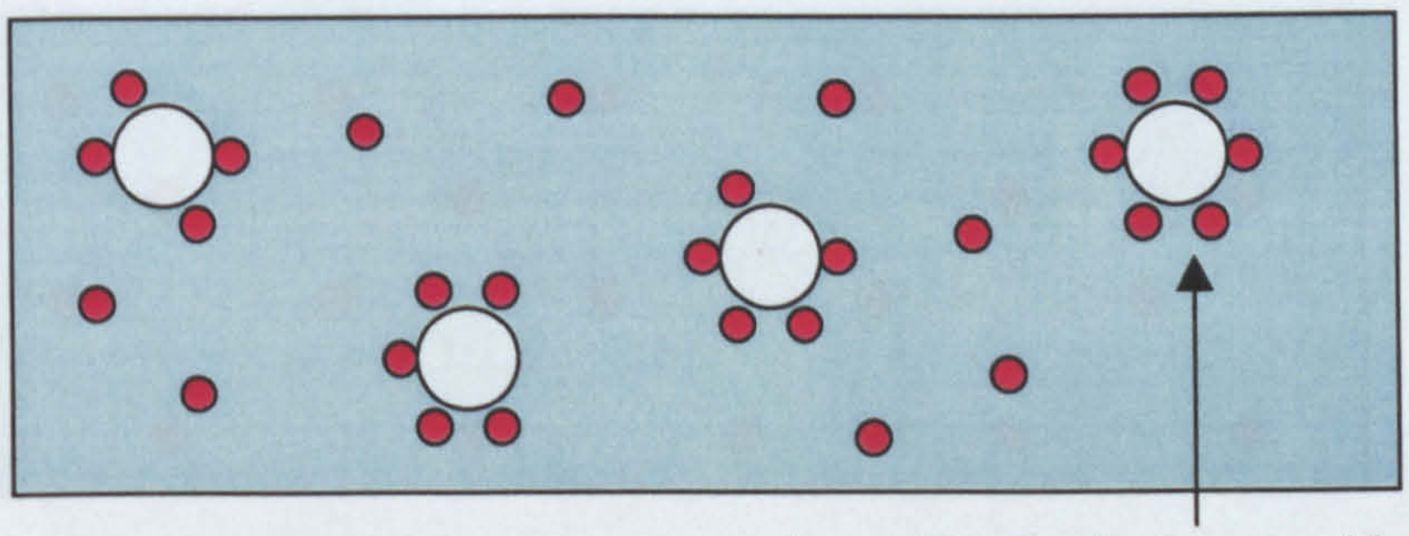
that interact with the dialysis membrane. Static sorption does not require the water-soluble polymer and adduct to be separated from the dye solution. The determination of the dye-binding constant for a water-insoluble polymer, K_S by static sorption is outlined in figure 1.9 [11].

Figure 1.9 Determination of K_S from static sorption

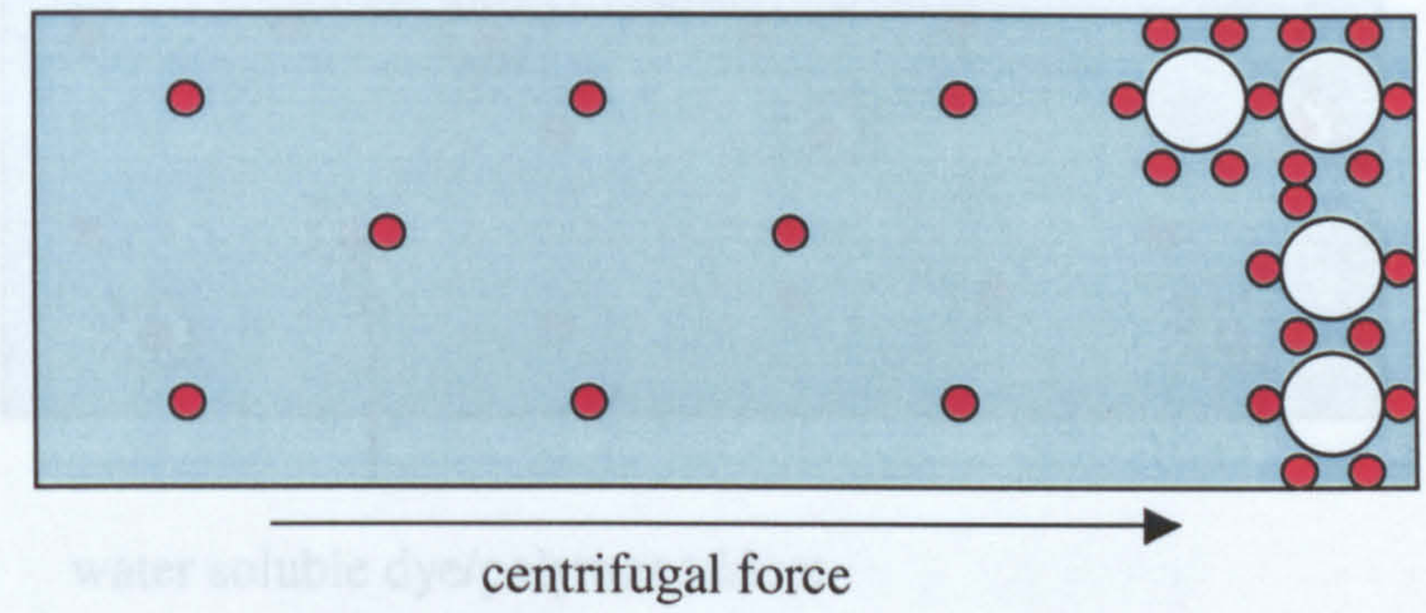
1) A known concentration dye stock solution is prepared and the absorption at its λ-max is recorded.



2) A known amount of water-insoluble cross-linked polymer is mixed into the dye stock. A proportion of the free dye binds at the surface of the water-insoluble polymer to form water-insoluble polymer/dye adducts.



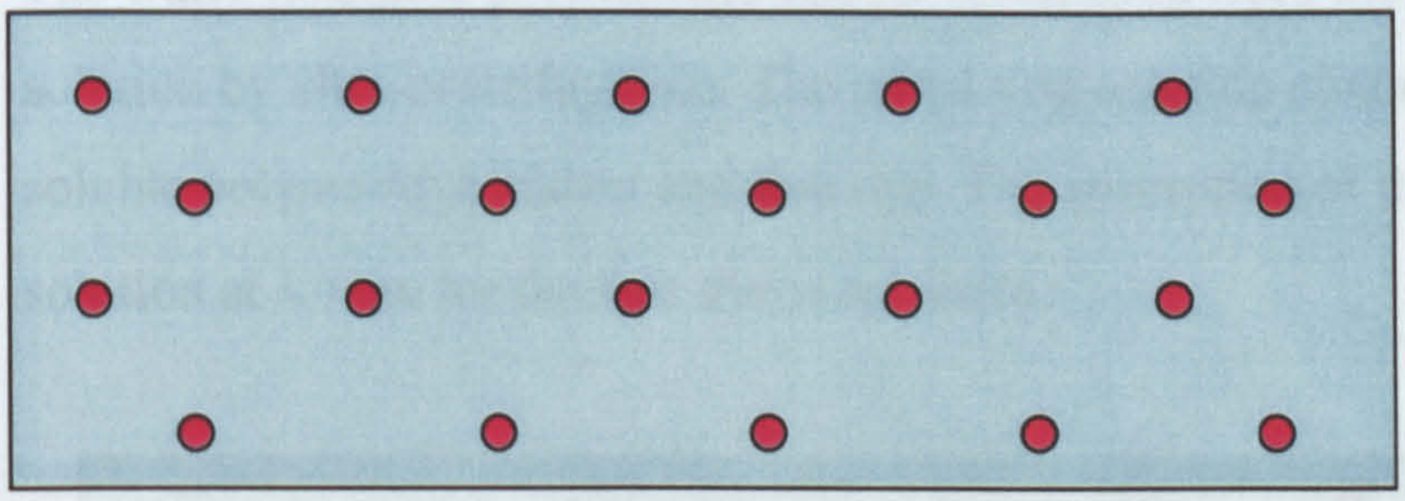
3) The water-insoluble polymer/dye adduct is removed from the dye solution by ultra-centrifugation. The λ-max absorption of the free dye remaining in the solution is recorded. This allows the calculation of the dye binding constant for the water-insoluble polymer, K_S.



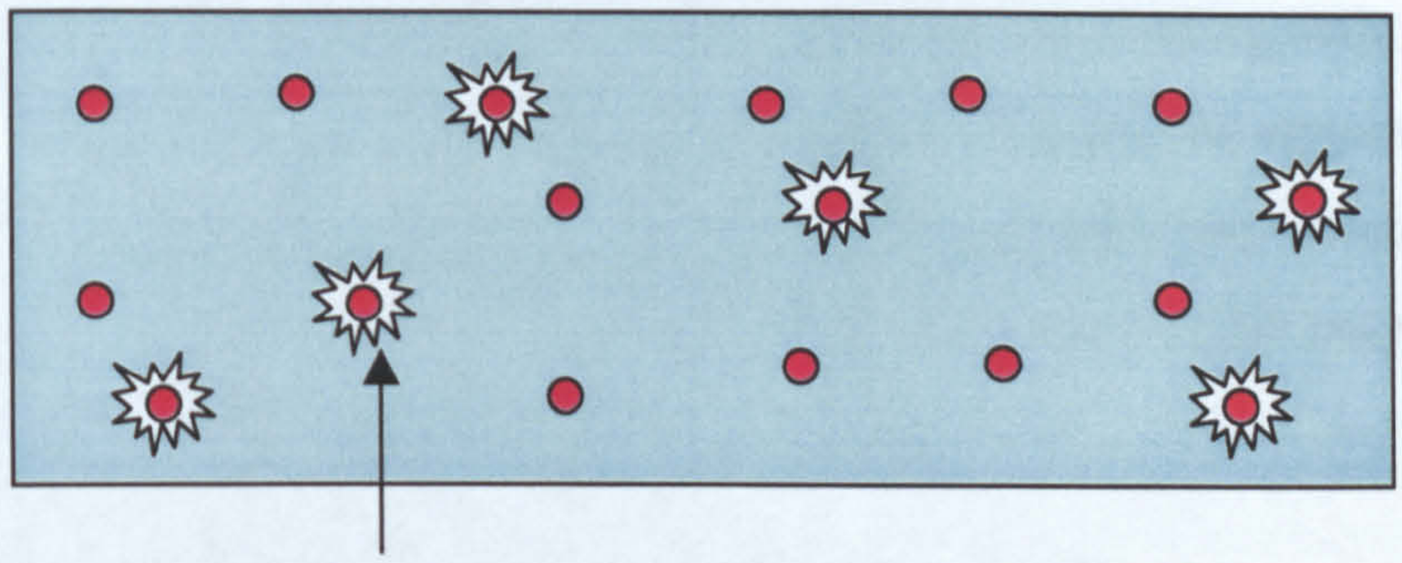
The dye-binding constant for a water-soluble polymer, K_P is calculated by performing a dye-binding experiment of the unknown water-soluble polymer together with a water-insoluble polymer of known dye-binding ability, K_S. Figure 1.10 illustrates a simplified representation of the method used for determining the dye-binding constant for a water-soluble polymer, K_P.

Figure 1.10 Determination of K_P from static sorption

1) A known concentration dye stock solution is prepared and the absorption at its λ-max is recorded.

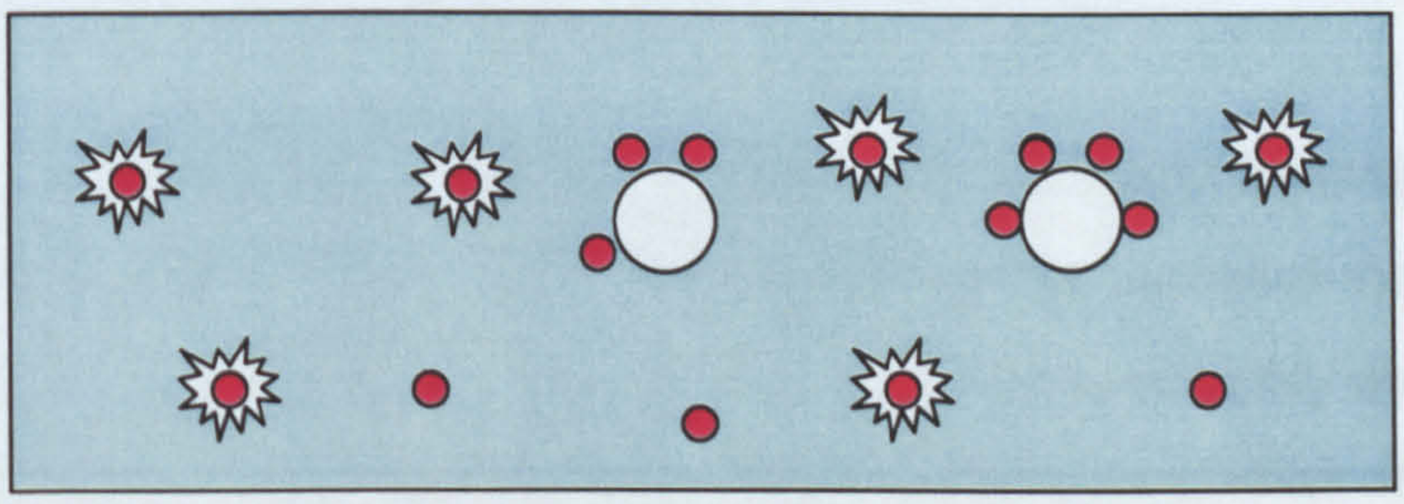


2) A known amount of water-soluble polymer is dissolved into the dye stock solution. A proportion of the free dye binds with the water-soluble polymer to produce water-soluble polymer/dye adducts. The absorption of a sample from the solution at the λ-max for the free-dye is recorded. Since the λ-max for the free-dye and the λ-max for the dye-polymer/adduct overlap this data must be calibrated with a known parameter, i.e., the binding ability with an insoluble polymer.

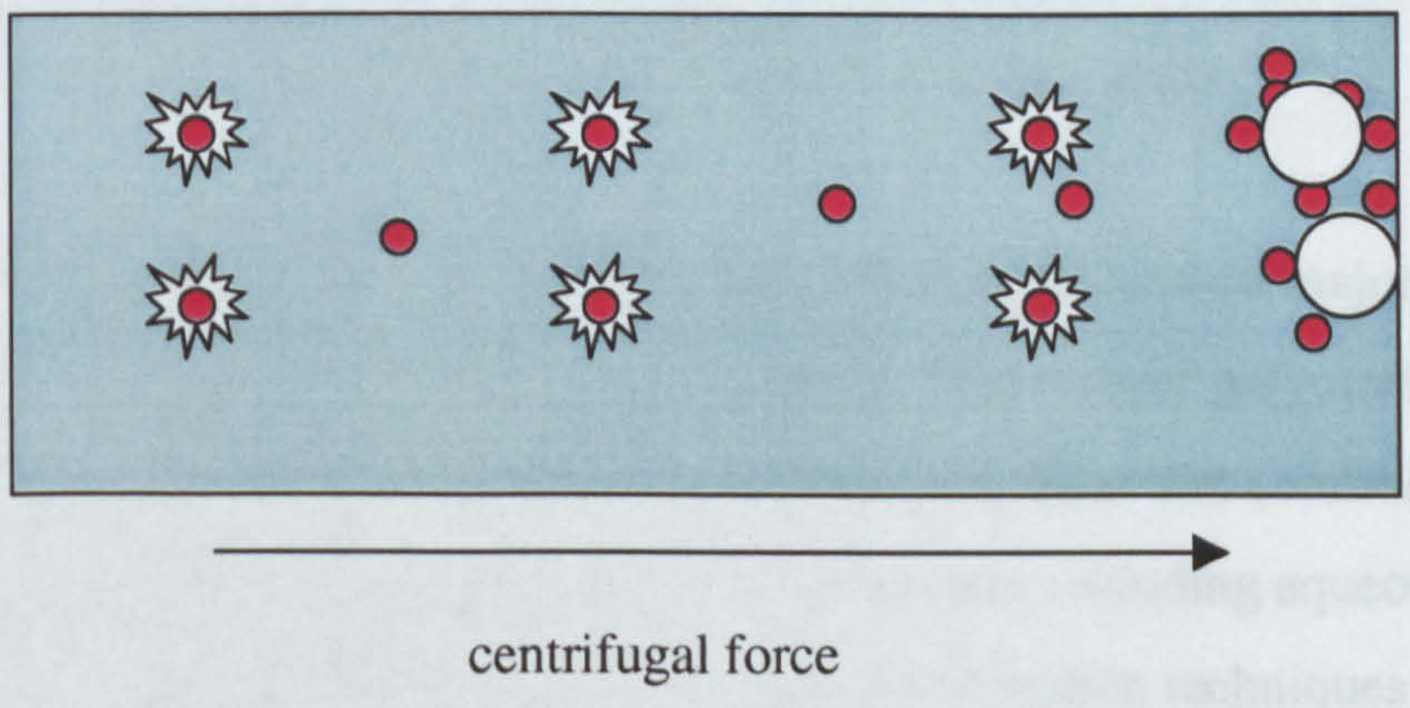


water soluble dye/polymer adduct

3) A known amount of cross-linked water-insoluble polymer is added to the solution. A proportion of the remaining free dye complexes with the water-insoluble polymer.



4) The water-insoluble polymer/dye adduct is removed from the dye solution by ultra-centrifugation. The remaining solution contains water-soluble polymer/dye adduct and free dye. The absorption of the solution at λ-max for the free dye is recorded.



centrifugal force

The loss of free-dye after the addition and removal of the water-insoluble polymer can be calculated. Taking into account the dye-binding ability of the water-insoluble polymer, K_S it is then possible to calculate the amount of free-dye that was present immediately after the addition of the water-soluble polymer. The value of the binding constant for the water-soluble polymer, K_P can then be calculated from these data.

1.3 SYNTHETIC POLYMERISATION

The selection of a synthetic method for a polymerisation process is based on several factors. These take into consideration the functionality and properties of the monomers, the desired properties of the polymer and importantly for industrial processes, the cost of the synthetic method used.

The demand for polymers in speciality applications has led to the development of new methods for polymer synthesis that enable greater control of the molecular weight distribution, conformation and architecture. Many novel chain-growth polymerisation techniques have been developed which allow for the synthesis of narrow polydispersity polymers that contain specific end group functionality and architecture [16-18]. Current commercially available anti-dye transfer agents are typically homopolymers or statistical co-polymers that are synthesised using free-radical polymerisation from monomers containing vinyl functionality. The polymerisation of vinyl based monomers by chain-growth procedures has been extensively researched over the past few decades and it is these methods of polymerisation that are of interest in this study [19-21].

For industrial processes, free-radical polymerisation offers several major advantages above all other chain-growth methods. Free-radical polymerisation is tolerant of monomer functionality and trace impurities. Reaction conditions are undemanding and a wide range of solvents can be used, including aqueous systems. Ionic, free-radical and co-ordination polymerisation techniques have all been developed to allow for control of architecture, functionality and molecular

weight distribution. The development of radical polymerisation techniques that provide inexpensive methods for controlled polymer synthesis has created routes to previously unobtainable polymers for use in the high volume market place. This introduction will review the principal methods of controlled free-radical polymerisation that have been developed. The polymerisation methods conducted in this research project have been based on conventional free-radical polymerisation and novel controlled radical polymerisation techniques.

1.4 FREE-RADICAL POLYMERISATION

The general reaction scheme for free-radical polymerisation was first proposed by Flory in 1953 and is now expressed using four distinct steps, these are: initiation, propagation, termination and chain-transfer [22]. The mechanisms and reaction kinetics for these different steps are important for understanding the structural and physical properties of polymers that are formed from radical polymerisations. This section provides a general review of the mechanistic steps for radical polymerisation and methods of control, all of these topics will be expanded upon in later chapters where a more detailed explanation is necessary.

1.4.1 Initiation

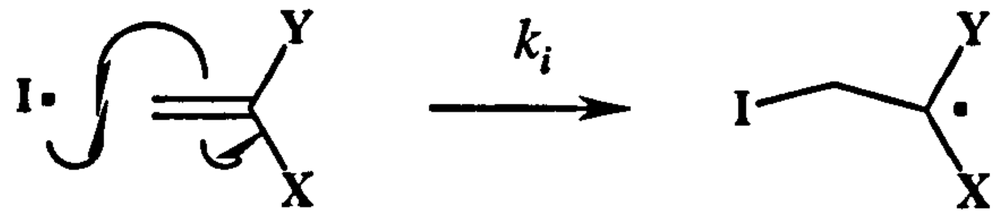
Initiation is a process that generates primary radicals that add to the vinyl group of the monomer to produce initiator-monomer adduct radicals that can then propagate. Commercial initiators typically decompose homolytically by thermolysis, photolysis or by redox reactions to yield primary radicals.

Figure 1.11 Decomposition of initiator

$$I_2 \xrightarrow{k_d} 2\,I\bullet$$

k_d is the rate constant for initiator decomposition

Figure 1.12 Initiation of monomer



Primary initiator radicals react with monomer to yield a propagating centre. k_i is the rate constant for initiation with monomer. With few exceptions the majority of radicals prefer to react with the least hindered end of an unsymmetrical vinyl group, this is known as tail addition.

The selection of an initiator for a polymerisation system is based on its suitability for use with the reaction conditions, monomers, solvents and additional components in the polymerisation system as well as any properties that may be imparted into the polymer product. Azo-compounds such as dialkyl diazenes, e.g. 2,2'-azo-bis-*iso*butyronitrile, AIBN (**1.9**) are common thermal initiators for free radical polymerisation. AIBN thermally decomposes to yield two carbon-centred cyano*iso*propyl radicals (**1.10**) and liberates 1 equivalent of molecular nitrogen. Figure 1.13 illustrates the decomposition mechanism for AIBN.

Figure 1.13 Decomposition pathway for AIBN

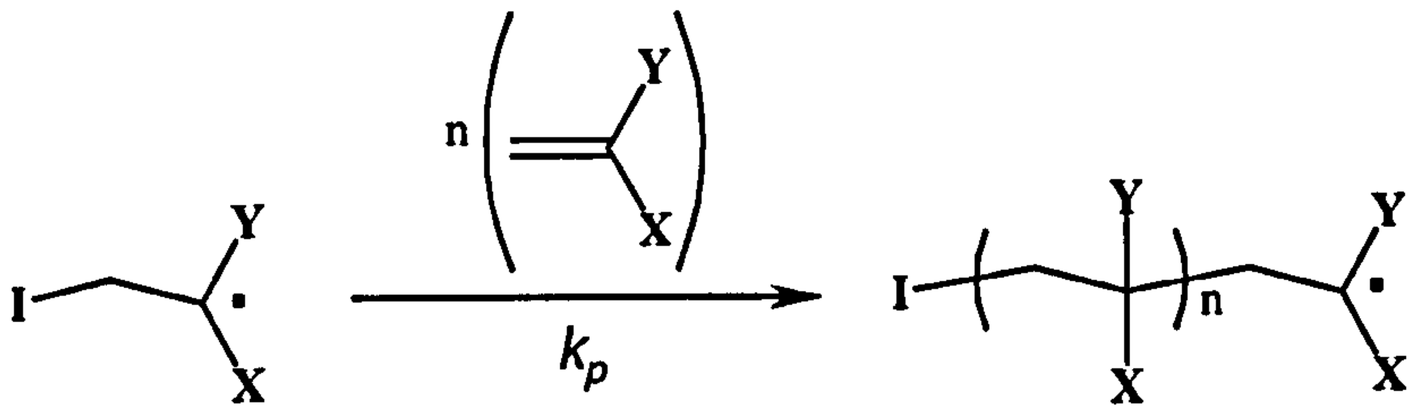
AIBN (**9**) cyano*iso*propyl radical (**10**)

The initiators that have been used in this study are thermal initiators based on dialkyl diazenes, azo compounds.

1.4.2 Propagation

Propagation in free-radical polymerisation consists of a series of additions of carbon-carbon vinyl groups to a radical centre. Figure 1.14 shows the preferred head to tail addition of monomer to a propagating chain.

Figure 1.14 Free-radical Propagation

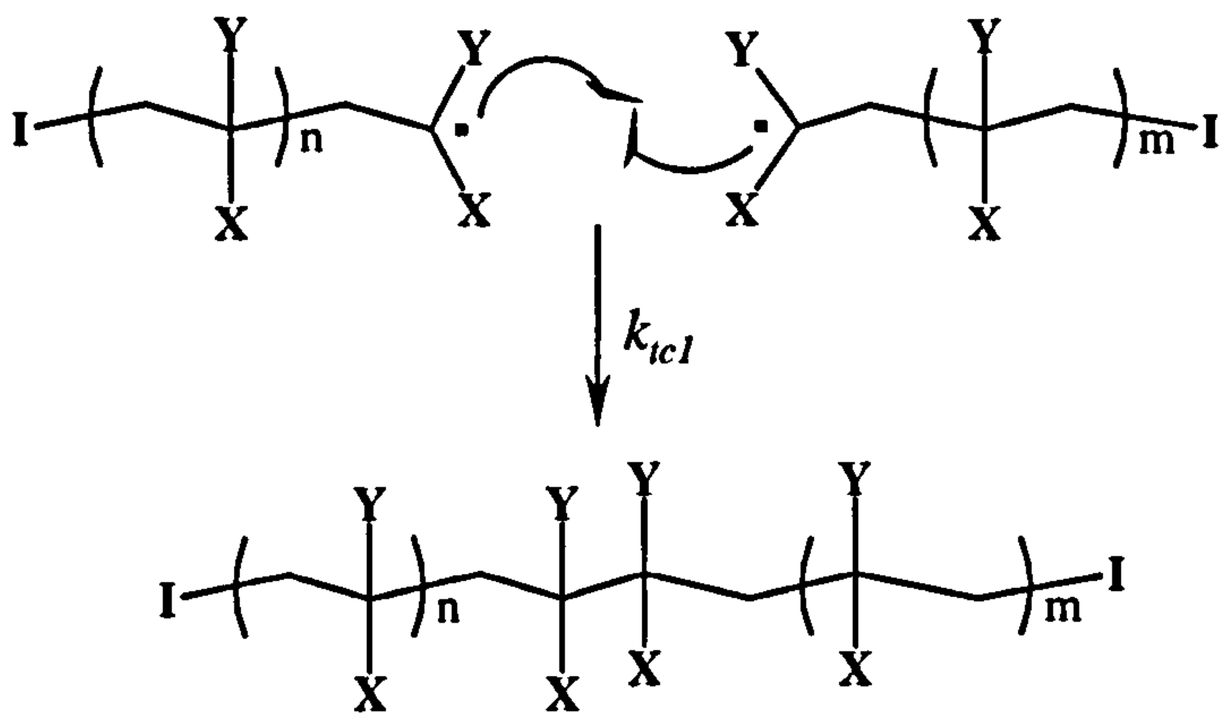


k_p is the rate constant for free-radical propagation. Propagation continues with the addition of monomer to the growing polymer chain until termination occurs.

1.4.3 Termination

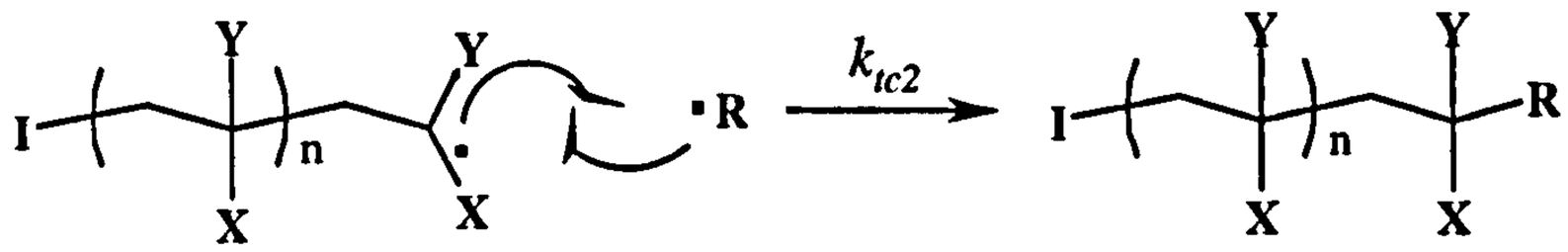
Termination is defined as the removal of a radical species from a propagating chain to yield a 'dead' polymer. Termination that results from radical-radical reaction may occur by three different pathways: combination of two propagating chains; the combination of a propagating chain with a primary radical; and disproportionation between two propagating chains.

Figure 1.15 Combination of two propagating chains



Termination by combination of two propagating chains occurs where two propagating radical centres combine together in a head to head linkage to form a 'dead' polymer chain.

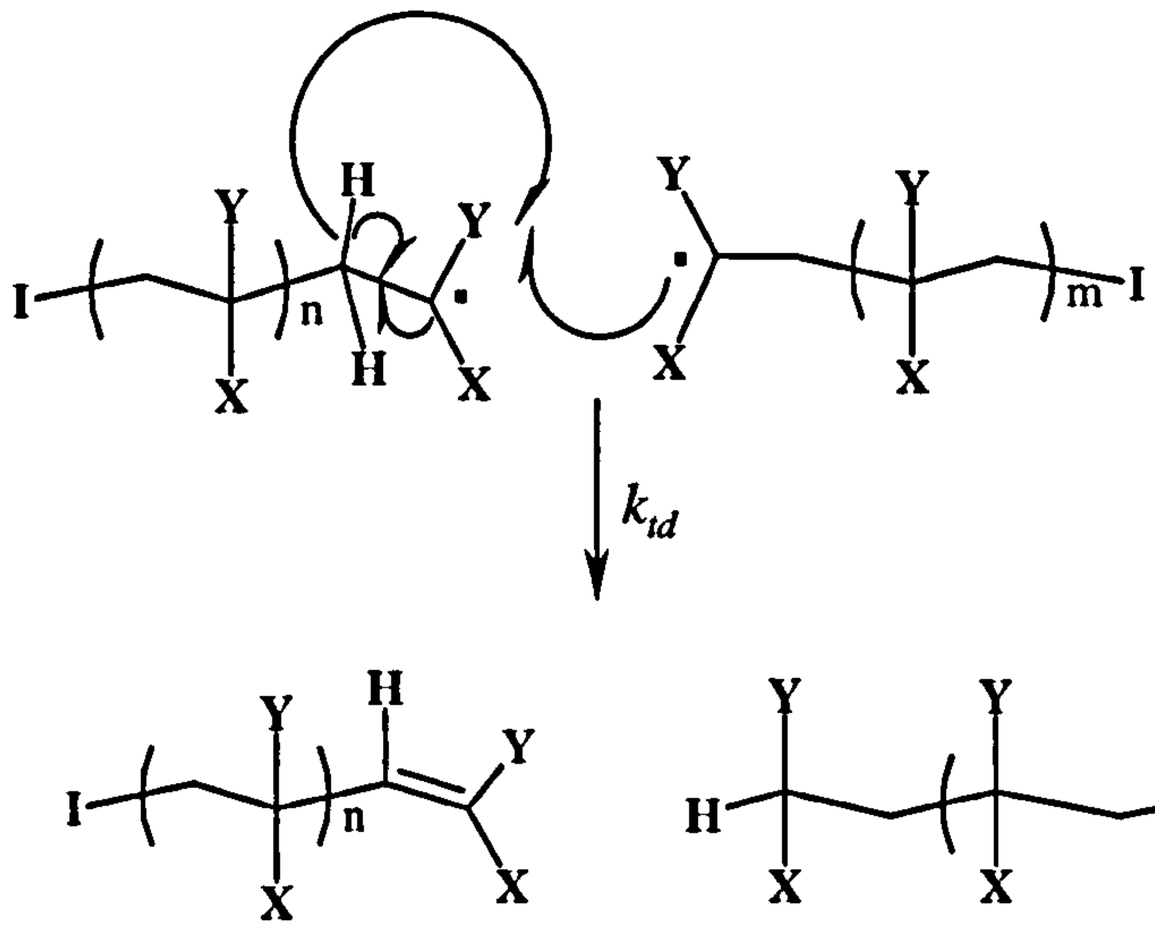
Figure 1.16 Combination of a propagating chain with a primary radical



The combined rate constant k_{tc} for termination by combination is given by the expression:

$$k_{tc} = k_{tc1} + k_{tc2} \qquad (1.6)$$

Figure 1.17 Disproportionation

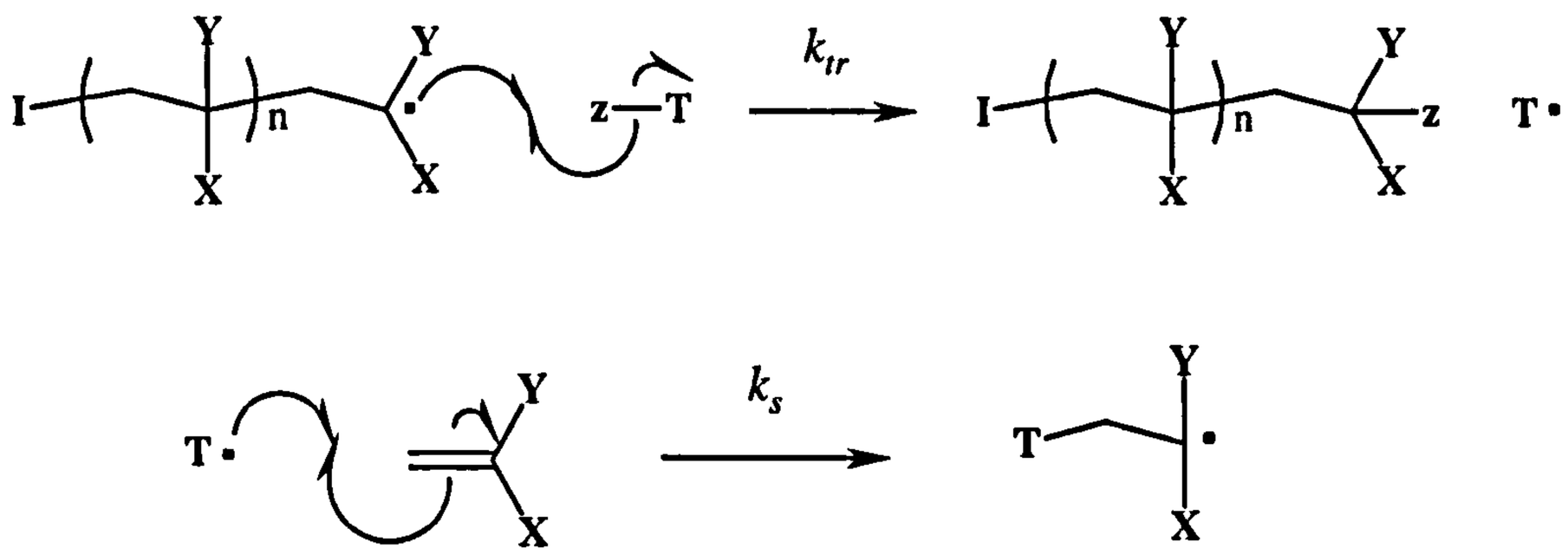


Termination by disproportionation occurs where one radical centre abstracts a hydrogen atom from the β position with respect to another radical centre, this process produces a vinyl terminated group on one chain end of the 'dead' polymer and a saturated end group on the other. The unsaturated product can react as a monomer in further propagation reactions and this introduces a degree of graft polymer impurity into systems where termination by disproportionation occurs.

1.4.4 Chain-Transfer

Chain-transfer can also be considered as a route by which termination can occur. Chain-transfer takes place when the reaction of a propagating centre occurs with another component in the reaction mixture. This may be solvent, monomer, initiator, polymer or a specifically added chain-transfer reagent. The transfer mechanism involves the transfer of an atom, or a group from the transfer agent to the propagating centre to yield a 'dead' polymer chain and a new propagating radical centre that is derived from the transfer agent. Figure 1.18 outlines the basic mechanism for chain-transfer.

Figure 1.18 Chain-transfer



In the absence of an added chain-transfer reagent in almost all free-radical polymerisation, transfer between initiator, monomer, polymer, and sometimes the solvent can occur. The addition of specific reagents that act as chain-transfer agents in free-radical polymerisation is discussed in section 1.5.1.

1.5 CONTROLLED RADICAL POLYMERISATION

In free-radical polymerisation control of the molecular weight distribution, architecture and end group functionality of polymers is based upon the development and manipulation of the termination pathways. Two different approaches have been pioneered over the past twenty years that provide methods of control for free-radical polymerisation, these are commonly known as chain-transfer mediated polymerisation and living polymerisation systems.

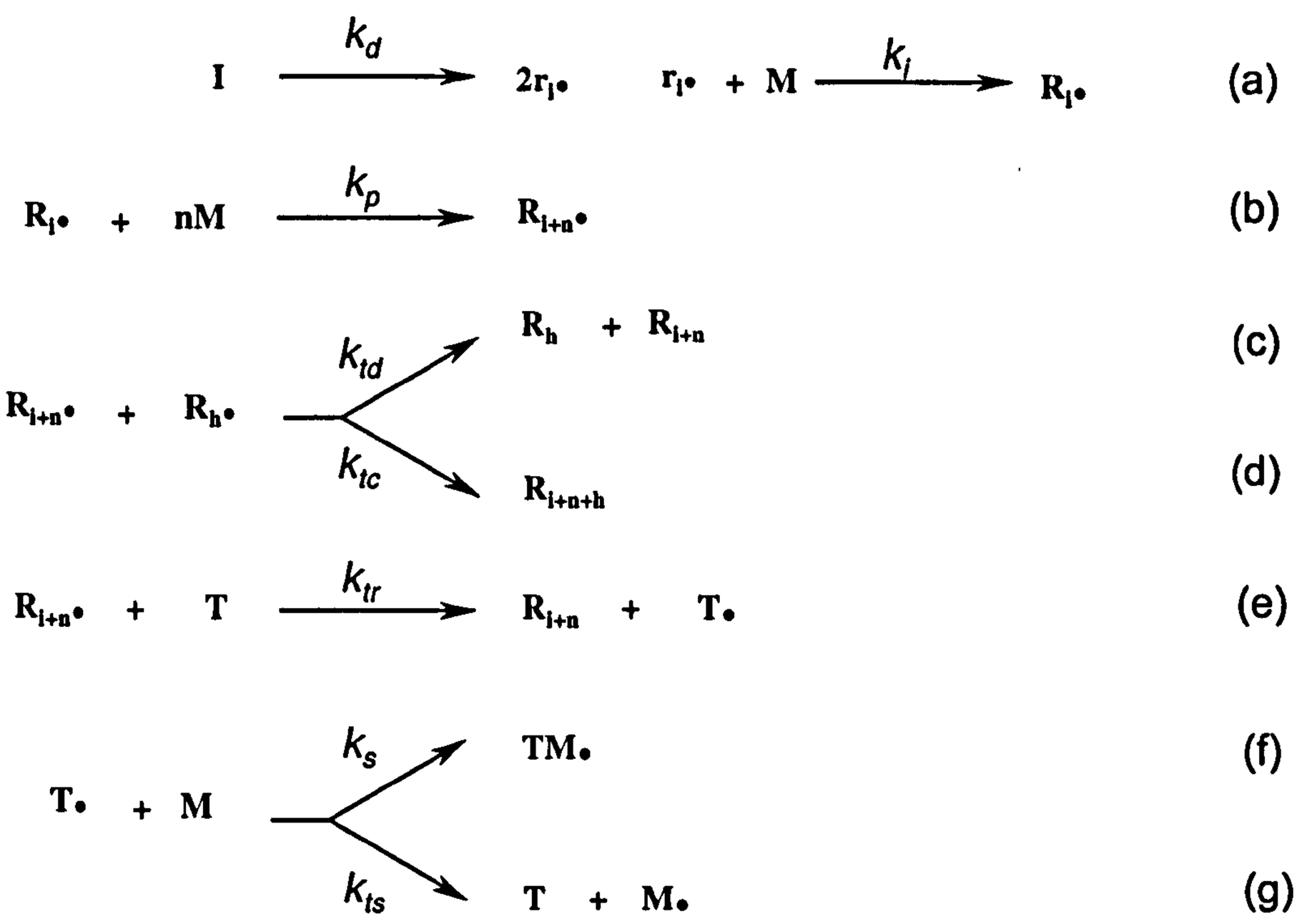
1.5.1 Chain-Transfer Mediated Polymerisation

Chain-transfer mediated polymerisation provides a simple method for the preparation of low molecular weight polymers and macromonomers. Chain-transfer mediated polymerisation does not, however, provide any control over

the polydispersity index of the sample which remains similar to that obtained from radical polymerisation.

The general reaction kinetics for a radical polymerisation in the presence of an added chain transfer agent, excluding those for transfer to polymer or initiator are given in Figure 1.19.

Figure 1.19 Kinetics of Chain-transfer mediated polymerisation



The nature and identity of the species involved together with the reaction conditions dictate the outcome of the transfer step. I is the initiator molecule, k_d is the rate constant for decomposition to produce the initiating radical species [r•]. k_i is the rate constant for initiation of monomer [M] to produce a propagating polymer [R*i*•]. k_p is the rate constant for propagation of the growing polymer with monomer chain to produce [R_{i+n}•]. Termination of the growing polymer [R_{i+n}•] by combination k_{td} and disproportionation k_{td} produces 'dead' polymer species. Transfer of the growing polymer chain [R_{i+n}•] to a transfer agent [T], where the rate constant for the transfer step is k_{tr} produces a 'dead' transfer product [R_{i+n}] and a new initiating radical [T•]. The new initiating radical can then react with monomer to produce either a propagating

combination product [TM•] or monomer can abstract the radical from the transfer species to form a new initiating monomer radical [M•] and regenerate the transfer species [T]

When the rate constant for re-initiation of monomer (k_s) is greater than or equal to the rate constant for propagation (k_p) then efficient chain-transfer will occur. The radical transfer product [T•] initiates the growth of new chains resulting in a reduction in the average molecular weight without altering the overall rate of polymerisation. The addition of a specific amount of chain-transfer agent during a polymerisation can be used to control the average chain length of the polymer. When the value of k_s is less than the value of k_p then the rate of polymerisation will be reduced and the probability of side reactions occurring will increase. Monomers which possess high k_p values such as vinyl acetate or methyl acrylate tend to exhibit a more pronounced reduction in the rate of polymerisation than do monomers with relatively low k_p values such as methyl methacrylate or styrene. According to equation (g), chain-transfer proceeds without the regeneration of the chain-transfer agent, which is eventually consumed as the reaction progresses.

1.5.1.1 Chain-Transfer Co-efficient

The ability of a particular transfer agent to induce a molecular weight reduction in a polymerisation process is quantified by the chain-transfer co-efficient (Cs). The Cs value for a polymerisation is defined by the Mayo equation that is derived as follows [23]:

The average degree of polymerisation (D_p) of a polymer formed through radical polymerisation can be expressed in terms of the relative rates of monomer consumption and polymer formation (termination) assuming that termination is only due to radical-radical reaction and chain transfer.

$$D_P = -\frac{\frac{d[M]}{dt}}{\frac{d[P]}{dt}} = \frac{R_P}{R_t + R_{tr}} \quad (1.3)$$

$$= \frac{k_P[M][P\bullet]}{2k_t[P\bullet]^2 + k_{tr}[T][P\bullet]} \quad (1.4)$$

Rearranging equation (1.4) to separate the expression in terms of transfer and radical-radical termination gives:

$$\frac{1}{D_P} = \frac{2k_t[P\bullet]}{k_P[M]} + \frac{k_{tr}[T]}{k_P[M]} \quad (1.5)$$

D_{P0} is the average degree of polymerisation of the polymer formed in the absence of any chain-transfer agent. Substitution of D_{P0} for the radical-radical termination component gives:

$$\frac{1}{D_P} = \frac{1}{D_{P0}} + \frac{k_{tr}[T]}{k_P[M]} \quad (1.6)$$

Introducing the chain-transfer co-efficient (Cs) provides a measure of the effectiveness of a chain-transfer agent at reducing molecular weight in a polymerisation, i.e., $Cs = k_{tr} / k_P$.

$$\frac{1}{D_P} = \frac{1}{D_{P0}} + Cs\frac{[T]}{[M]} \quad (1.7)$$

Equation 1.7 is known as the Mayo equation.

The effective chain-transfer co-efficient (Cs) of different transfer agents is dependent upon the relative reactivity with monomer and transfer agent under the specific reaction conditions. Experimentally, Cs is determined through the polymerisation of a series of monomer stock solutions containing different

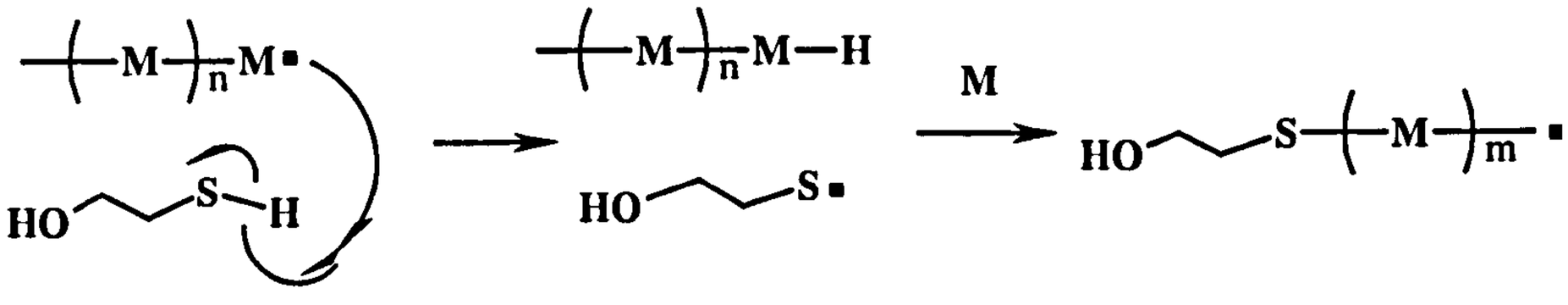
amounts of transfer-agent. One sample usually contains no transfer-agent allowing the value of D_{p0} to be calculated. Each polymerisation is run to a low conversion to eliminate errors due to the changes in monomer to transfer agent concentration. A plot of $(1/D_P)$-$(1/D_{p0})$ versus [T]/[M] yields a linear graph with a gradient equal to the value of Cs that passes through the origin.

1.5.1.2 Chain-transfer agents

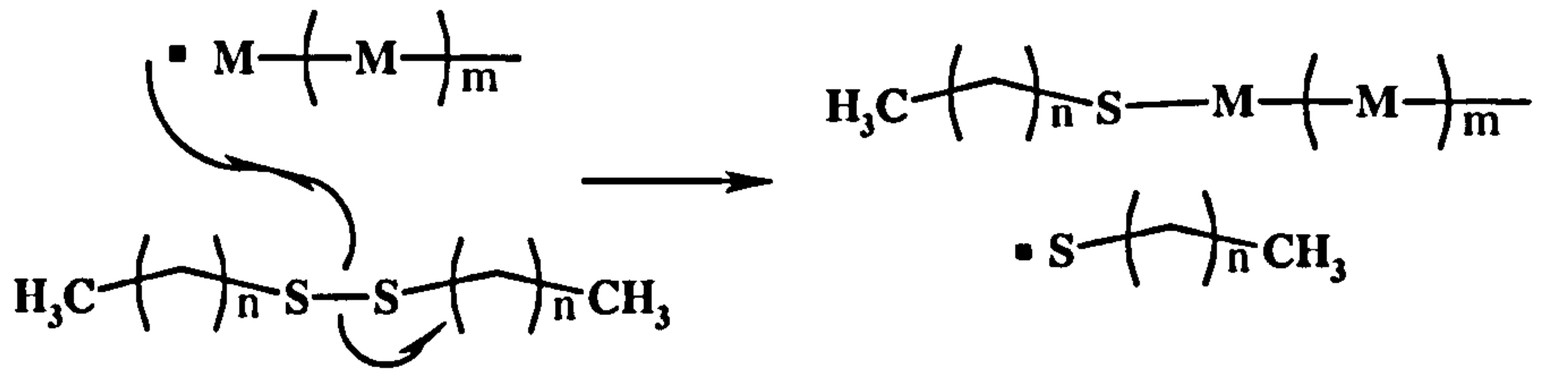
Thiols [24]and disulfides [25] are classic examples of chain-transfer agents providing reduction in molecular weight for radical polymerisations. Terminal functionality at the ω-end of the polymer and α,ω-terminal functionality in the polymer, otherwise known as telechelic functionality can be introduced into the 'dead' polymer through the use of specific functionalised transfer agents. Figure 1.20 illustrates some industrially important chain-transfer agents and their transfer products.

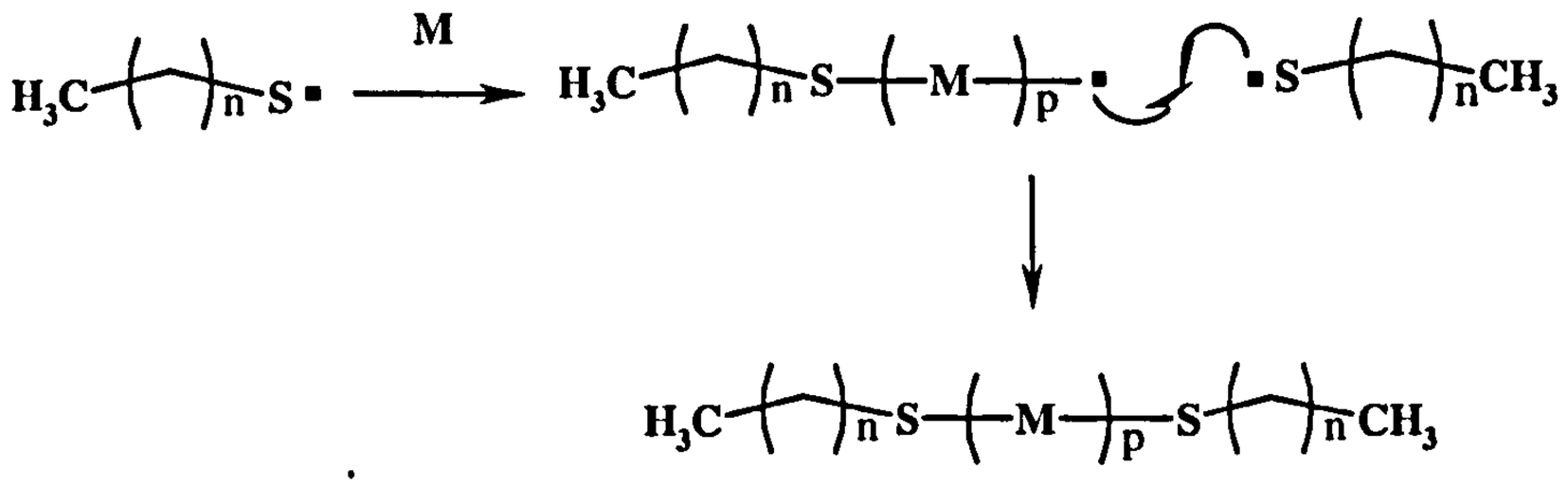
Figure 1.20 Chain-Transfer Agents

Thiols, general formula: RSH such as mecaptoethanol are useful as transfer agents leading to α-functional polymers.



Disulfides, general formula: RSSR such as dialkyl disulfides act as transfer agents leading to α,ω-functional polymers





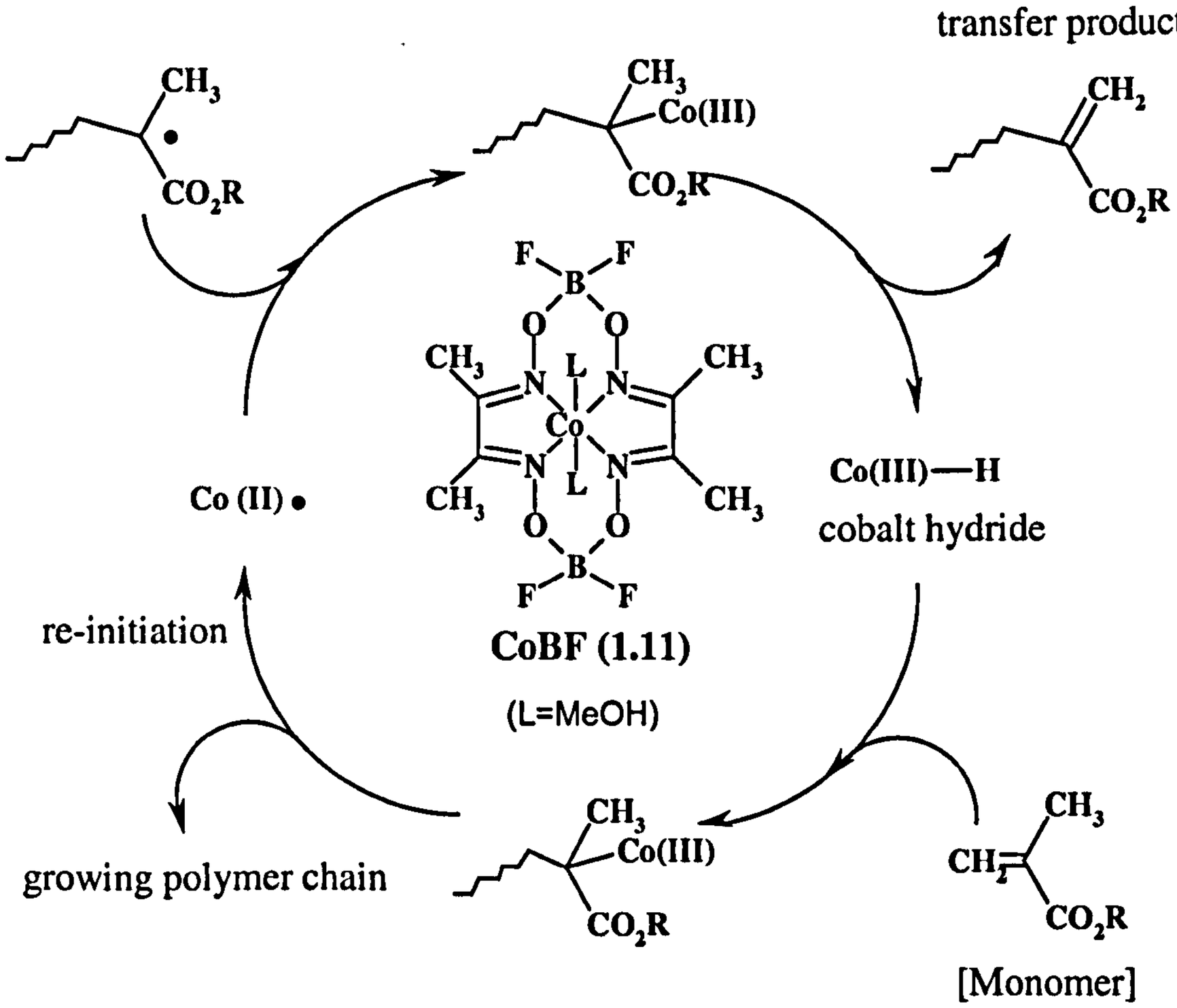
The terminal C-S bond that results from transfer to a disulfide transfer agent provides a route for the synthesis of block co-polymers. Specific disulfides lead to products where the terminal C-S bond is relatively weak and is susceptible to homolytic, thermal or radical induced cleavage thus producing end groups that can initiate block co-polymerisation.

Thiols, disulfides and other traditional chain transfer agents have a relatively low chain transfer activity (Cs) ~1. This means that large amounts of transfer agent are often required for effective molecular weight reduction to be attained. The industrial application of chain transfer agents is limited due to the relatively high cost of the transfer agent and also due to the poor reactivity of transfer agents with specific monomer types, e.g., methyl methacrylate with aliphatic disulfides.

1.5.1.3 Catalytic Chain-Transfer Polymerisation (CCTP)

The development of an industrially applicable chain-transfer agent that is regenerated during the polymerisation process was first introduced by Enikolopyan *et al* in 1981 with the use of low spin Co(II) porphyrin complexes [26,27]. Agents that are regenerated during the polymerisation process are known as catalytic chain-transfer agents (CCTAs). Over the past few decades a number of CCTAs derived from low spin Co(II) macrocycles have been developed [28,29]. The most widely used CCTA is [Bis[μ-[(2,3-butanedione dioximato)(2-)-O:O']] tetrafluorodiborato(2-)-N,N',N'',N''']] cobalt (CoBF) **(1.11)**. Figure 1.21 outlines a simplified catalytic cycle for the catalytic chain-transfer mediated polymerisation (CCTP) of a methacrylate derived monomer with CoBF.

Figure 1.21 CCT cycle of methacrylate monomer with CoBF (1.11)



Complexation of the Co(II) macrocycle with the radical centre of the propagating polymer chain end produces an alkyl Co(III) intermediate. Intramolecular β–hydrogen transfer at the terminal chain end to the Co(III) macrocycle yields a terminally unsaturated macromonomer and Co(III) hydride. The Co(III) hydride re-initiates polymerisation with either monomer or macromonomer through addition across the vinyl group. Traditional chain-transfer agents such as thiols have been shown to have a Cs for the bulk polymerisation of methyl methacrylate (MMA) of ~1. This can be compared with the value of Cs in the CCT mediated polymerisation of MMA in bulk with CoBF, which has a Cs value of ~40 000 [28,30]. The high transfer activity and the catalytic nature of the transfer agent means that only parts per million (ppm) quantities of CCTA are required with respect to monomer for effective molecular weight reduction to be obtained with methacrylate derived monomers. CCTP with other monomer types is more complicated; slow poisoning of the catalyst is observed for CCTP with styrene and acidic monomers [26,31].

1.5.2 Living Polymerisation

Szwarc first introduced the terminology of a 'living' polymer to describe a polymerisation performed in a non-protic apolar solvent where no transfer to solvent or termination was possible [8]. For a living polymerisation system $k_p >> k_t$, which means that all chains propagate throughout the reaction until a mode of termination is introduced. The definition of an ideal 'living' polymerisation system is one where no mode of termination is available, i.e., $k_t = 0$. To establish control of molecular weight in a living system instantaneous initiation of the monomer is required, this results in all chains growing uniformly during the reaction. All of the polymer chains will therefore have similar degrees of polymerisation at any given time and consequently living polymerisation can produce polymers with a very narrow polydispersity (PDi ~1.1) in some cases. The molecular weight of a living polymer synthesised from a mono-functional initiating species can therefore be calculated according to equation 1.8.

$$\overline{M}_n = \left(\frac{[M]}{[I]} \times conversion \times M_{mon} \right) + M_{init} \qquad (1.8)$$

Where: [M] is monomer concentration, [I] is initiator concentration, M_{mon} is the relative molecular mass of the monomer and M_{init} is the relative molecular mass of the initiating species.

Living polymerisation systems were first introduced for anionic, cationic and co-ordination techniques [19,32]. Conventional anionic, cationic and co-ordination procedures are expensive. They require ultra-pure reagents, inert and dry solvents together with extreme conditions. The adaptation of conventional organic synthetic reactions for carbon-carbon bond formation has lead to the development of methods of control for novel pseudo-living radical systems. For living radical polymerisation to be efficiently performed the number of incidences of radical-radical termination reactions must be practically zero: to achieve this, reversible termination of the propagating chain is introduced.

Three different methods for establishing reversible chain termination in radical polymerisation reactions have been described in the literature: Stable Free Radical Polymerisation (SFRP) [33-35] , Atom-Transfer Polymerisation (ATP) or Atom Transfer Radical Polymerisation (ATRP) [36-40], and Reversible Addition-Fragmentation Transfer (RAFT) [41,42]. Living polymerisation not only provides a route for the synthesis of well-defined homopolymers but also the preparation of polymers with controlled conformation and architecture including block co-polymers and star polymers [43,44]. For a living radical homopolymerisation in which all of the monomer is consumed the transfer agent will terminate all polymer chains. The use of these chains as macroinitiators for block co-polymerisation is possible with suitable reaction conditions where the macroinitiator regenerates the transfer species and re-establishes the living polymerisation of the co-monomer. The syntheses of specific molecular weight polymers with narrow polydispersity, typically PDi < 1.3, can be achieved by careful selection of the transfer species and through manipulation of the relative concentrations of monomer and initiator. Homopolymerisation of monomer [A]

followed by purification and subsequent reaction of the product homopolymer as a macroinitiator with monomer [B] will result in a well-defined [A]-[B] block co-polymer. Similarly, the use of a core molecule containing more than one initiating site can be used to synthesise more complex products including star polymers.

1.5.1.1 Stable Free Radical Polymerisation (SFRP)

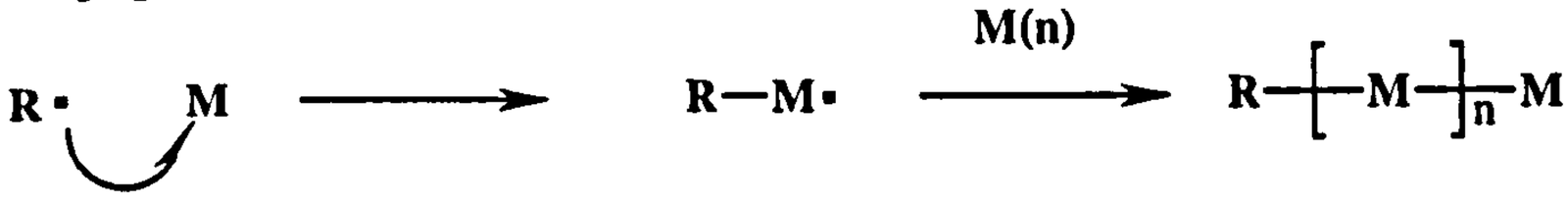
Stable free-radical species that are unable to initiate polymerisation of monomers are used to control radical polymerisation by promoting the reversible capping of the growing polymer chain. Initiators that are used to generate stable free-radical species in controlled radical systems where reversible chain termination is established are known as 'Iniferters'. The term iniferter was introduced by Otsu and Yoshida and is derived from *Ini*tiator, Trans*fer* Agent and Chain *Ter*minator. Figure 1.22 outlines a simplified mechanism for iniferter mediated living polymerisation [45].

Figure 1.22 Iniferter controlled living polymerisation

1) Decomposition of Iniferter

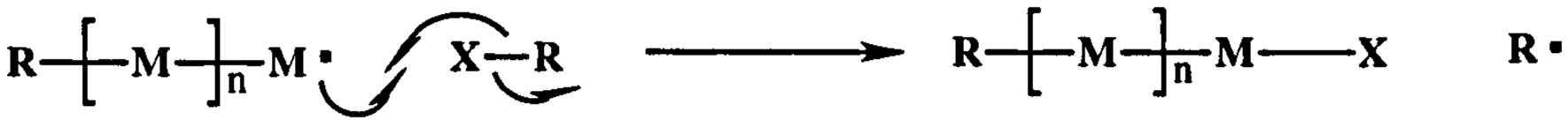
Where X• is a stable, long-lived radical that is unable to initiate polymerisation.

2) Propagation



3) Primary radical termination/initiation

4) Transfer to Iniferter



Step 3 dramatically decreases the number of propagating radical species and therefore both the frequency of radical-radical termination and the rate of polymerisation are reduced.

Iniferters that are used in living radical polymerisation require the following properties:

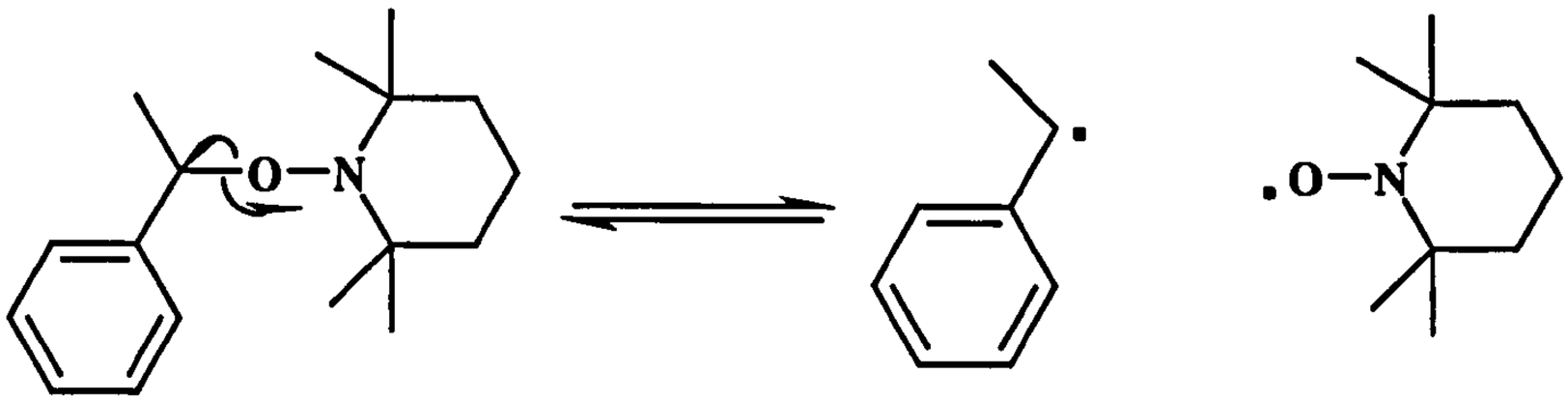
1) The decomposition of initiator should yield at least one long-lived, free radical that should be slow, or unable, to initiate polymerisation
2) Termination of primary radicals and termination with initiator should be the only significant pathways for the reduction of chain growth. Termination of primary radicals must occur by combination with transfer to initiator and must only occur through a group transfer mechanism
3) Reversible homolysis of the end group (X) to regenerate the propagating radical species must readily occur under the reaction conditions.

Several different classes of compounds are known to be effective iniferter species, of which organosulfur compounds, alkoxyamines and organocobalt macrocycles are typical examples. Alkoxyamine derived systems are widely favoured as they offer significant advantages over the other agents.

Alkoxyamines are inert towards most monomer types and are not susceptible to decomposition under the reaction conditions. Alkoxyamines are formed from the reaction of an appropriate nitroxide species with a carbon-centred radical. Nitroxide species do not directly initiate radical polymerisation. Figure 1.23 outlines the formation of a common nitroxide iniferter species: 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (**1.14**). The homolytic decomposition of a styrene derived alkoxyamine species, 2,2,6,6-tetramethyl-1-(1-

phenylethoxypiperidine) (TEMPO-Sty) (**1.12**) yields the stable TEMPO nitroxide radical (**1.14**) and the styrene based, 1-phenylethyl initiating radical (Sty•) (**1.13**).

Figure 1.23 Stable TEMPO free radical species



TEMPO-Sty (**1.12**) Sty• (**1.13**) TEMPO (**1.14**)

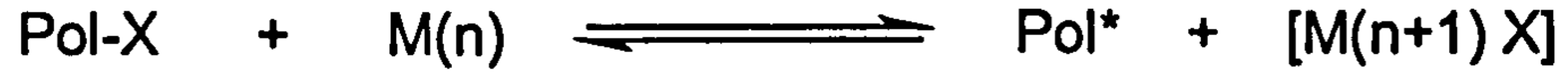
Many recent papers have investigated the use of stable nitroxide radicals for use in living polymerisation systems [35,46]. Moad and Solomon first described an effective nitroxide mediated living polymerisation of styrene and to yield well-defined and low polydispersity polymers. Nitroxide-mediated polymerisation systems are relatively simple when compared with atom transfer polymerisation (ATP) [34]. They do not contain metal complexes and this leads to the simplified purification of the product polymer. The syntheses of narrow block co-polymers from nitroxide-mediated processes are limited to use with styrene and acrylate based macroinitiator systems and are shown to be ineffective for methacrylate monomers. Tertiary centred alkoxyamine species such as methacrylates are unable to self-initiate and it is this phenomenon that reduces the equilibrium constant for the formation of primary radicals and therefore prevents the synthesis of narrow block co-polymer products.

1.5.1.2 Transition Metal Mediated Living Radical Polymerisation or Atom Transfer Polymerisation (ATP)

Transition metal mediated living radical polymerisation was introduced by Sawamoto and by Matyjaszewski in 1995 [36,37]. This is a development of the important organic synthetic reaction for carbon-carbon bond formation: atom-

transfer radical addition (ATRA) [47,48]. ATRA occurs where a halogen atom is transferred from an alkyl halide species [R-X] to a transition-metal catalyst [M(n)] to form an oxidised [M(n+1)X] species and an [R•] radical. Rapid reaction between the new [R•] radical and a vinyl group [CH_2=CHR'] yields a radical addition intermediate [CH_2R-CHR'•]. The metal halide species can then donate the halogen atom to the radical intermediate species to form a saturated product [CH_2R-CHR'X] and to reform the metal catalyst [M(n)]. The rapid reaction between the metal halide and the vinyl group inhibits bimolecular termination between carbon-centred radicals and introduces a halide functionality into the addition product. When the addition product [CH_2R-CHR'X] can readily undergo a reversible halogen transfer to the transition-metal complex then ATRA can be successfully used as a method to control radical polymerisation. When a fast exchange process exists between halide donation and abstraction from the propagating polymer to the metal complex then a reversible capping of the growing polymer chain is established. Altering the position of this equilibrium provides control over the rate of monomer insertion. Figure 1.24 illustrates the simplest representation for the mechanism of atom-transfer polymerisation (ATP).

Figure 1.24 Atom-Transfer polymerisation



Pol* represents the active propagating polymer chain, n is the formal oxidation state of the metal complex and X is the halogen atom.

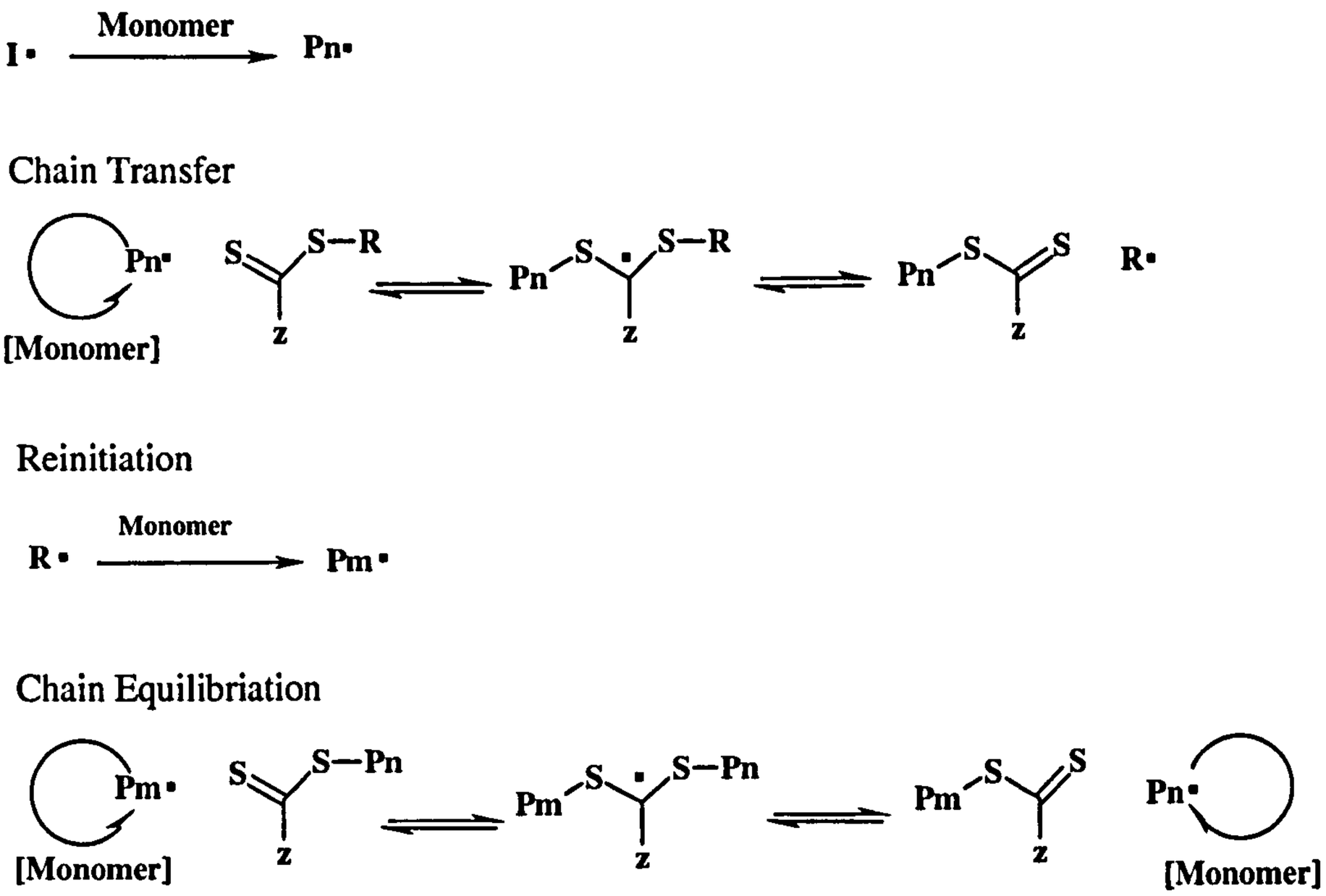
Matyjaszewski *et al* have pioneered a system that uses Cu(I)X together with two co-ordinating 2.2'-bipyridine (bpy) ligands as a catalyst in conjunction with an alkyl halide initiator [38,49-52]. Sawamoto *et al* have developed an analogous system based on a Ru(II)Cl_2-PPh_3 catalyst [36,53-55]. Over the past few years a wide number of different metal, ligand and initiator based systems have been developed for use with specific monomer types. Metals that have been successfully used in ATP include: Ni(II) [56,57] , Fe(II) [58], Pd(II) [59] and Rh(III) [60].

ATP can be used for the preparation of low polydispersity polymers (1.1 < PDi < 1.3) of methacrylates, acrylates and styrenes. Atom-transfer polymerisation systems have found widespread use in the syntheses of well defined block and architecturally controlled polymer species [43,44]. The large variety of functional alkyl halide initiating species that are readily available allows the rapid preparation of polymer species that were previously unobtainable. Polymers based on sugar and cholesterol initiators have recently been reported [61]. Problems associated with ATP include the difficulty in the removal of the catalyst from the polymer product and incompatibility with acid containing monomers (e.g., methacrylic acid) [62]. Due to the relatively high cost of the metal catalysts, and their subsequent discolouration of the product, a large amount of research is currently concerned with the development of systems that allow for the efficient recovery of the catalyst.

1.5.1.3 Reversible Addition-Fragmentation Transfer (RAFT) Polymerisation

Moad and Rizzardo introduced a new method for establishing living radical polymerisation in 1998: the reversible addition-fragmentation transfer (RAFT) process [42]. The application of certain thiocarbonylthio compounds as effective, reversible, addition-fragmentation chain-transfer agents was shown to promote living polymerisation with unprecedented flexibility in the use of different monomer and solvent systems. The mechanism for the RAFT polymerisation of a vinyl monomer in the presence of a generic thiocarbonylthio transfer agent is given in Figure 1.25.

Figure 1.25 Reversible addition-fragmentation transfer (RAFT) polymerisation.



Initiation of the monomer yields a growing polymer chain [P_n•]. Reaction of the growing polymer chain with a thiocarbonylthio transfer agent [S=C(Z)S-R] produces a new carbon-centred radical [R•] and a polymeric thiocarbonylthio compound [S=C(Z)S-P_n]. Re-initiation of the monomer by [R•] produces a new growing polymer chain [P_m•]. An equilibrium is established between the dormant polymeric thiocarbonylthio compound [S=C(Z)S-P_n] and the growing polymer chain [P_m•] with the equivalent polymeric thiocarbonylthio [S=C(Z)S-P_m] and the growing polymer chain [P_n•]. The rapid and reversible transfer of the polymeric thiocarbonylthio compounds with the growing polymer chains controls the rate of monomer addition, thus establishing living polymerisation. Since the majority of chains produced from RAFT polymerisations are terminated with thiocarbonylthio functionality, polymerisation with a second co-monomer can be performed to prepare block co-polymer species for a large range of different monomer types. For successful A-B block co-polymerisation to be performed in a batch

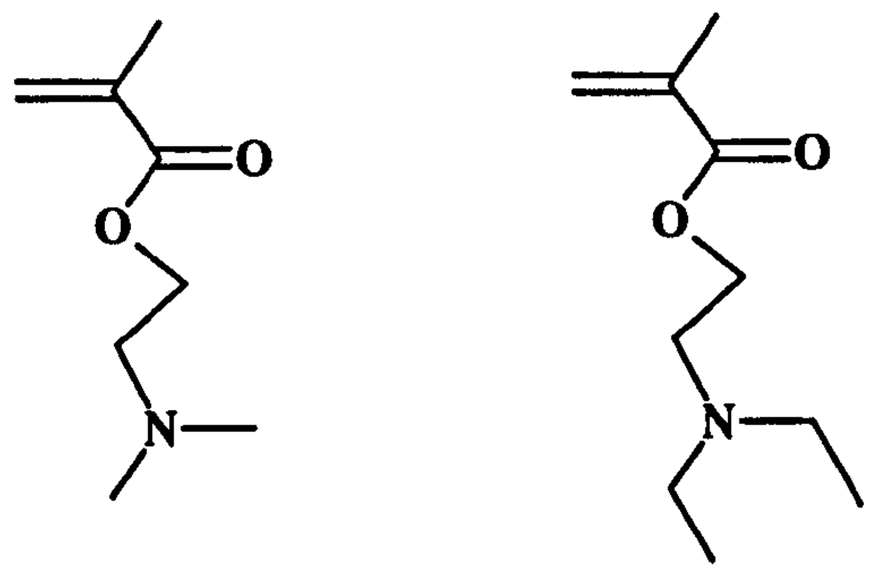
polymerisation process the polymeric thiocarbonylthio compound that represents the [A] block should have a high transfer constant with the propagating radical [B•]. The propagating radical [A•] should therefore be a better or comparable leaving group from the thiocarbonylthio species when compared with the [B•] radical. Styrene and acrylate polymeric thiocarbonylthio compounds have low transfer constants when compared with methacrylates, it is therefore essential that the methacrylate block is always prepared as block A. Chong *et al* have recently reported the syntheses of narrow controlled molecular weight block co-polymers including styrene-block-dimethacrylamide, butyl acrylate-block-acrylic acid, methyl methacrylate-block-2-(dimethylamino)ethyl methacrylate and methyl methacrylate-co-methacrylic acid [63]. These results clearly demonstrate the versatility of the RAFT process with the polymerisation of methacrylate and styrene monomers containing basic and acidic functionality.

1.6 TARGET POLYMERS AND METHODOLOGIES

The aim of this research project is to investigate how structural and chemical properties affect the dye-binding ability of synthetic polymers and to develop a novel, low cost anti-dye transfer agent with controlled conformation and architecture that exhibits improved dye-binding performance when compared with PVP. The choice of the monomers used to provide anti-dye transfer activity and hydrophilic character is limited by the methods of control that are currently available. The methods of control that have been utilised are; catalytic chain-transfer polymerisation (CCTP); atom transfer polymerisation (ATP); and, reversible addition-fragmentation transfer (RAFT) polymerisation. Monomers that are compatible with all of these techniques include styrene and methacrylate derivatives. Current commercially available anti-dye transfer agents are all based on nitrogen heterocycles. This body of research has focused on the development of novel anti-dye transfer agents containing the tertiary amine

functionalised methacrylate monomers: 2-(dimethylamino)ethyl methacrylate (DMAEMA) (**1.15**) and 2-(diethylamino)ethyl methacrylate (**1.16**). DMAEMA is a hydrophilic tertiary amine functionalised methacrylate and DEAEMA is a hydrophobic tertiary amine functionalised methacrylate. Polymers composed of these monomers have been shown to have interesting aqueous phase behaviour [2].

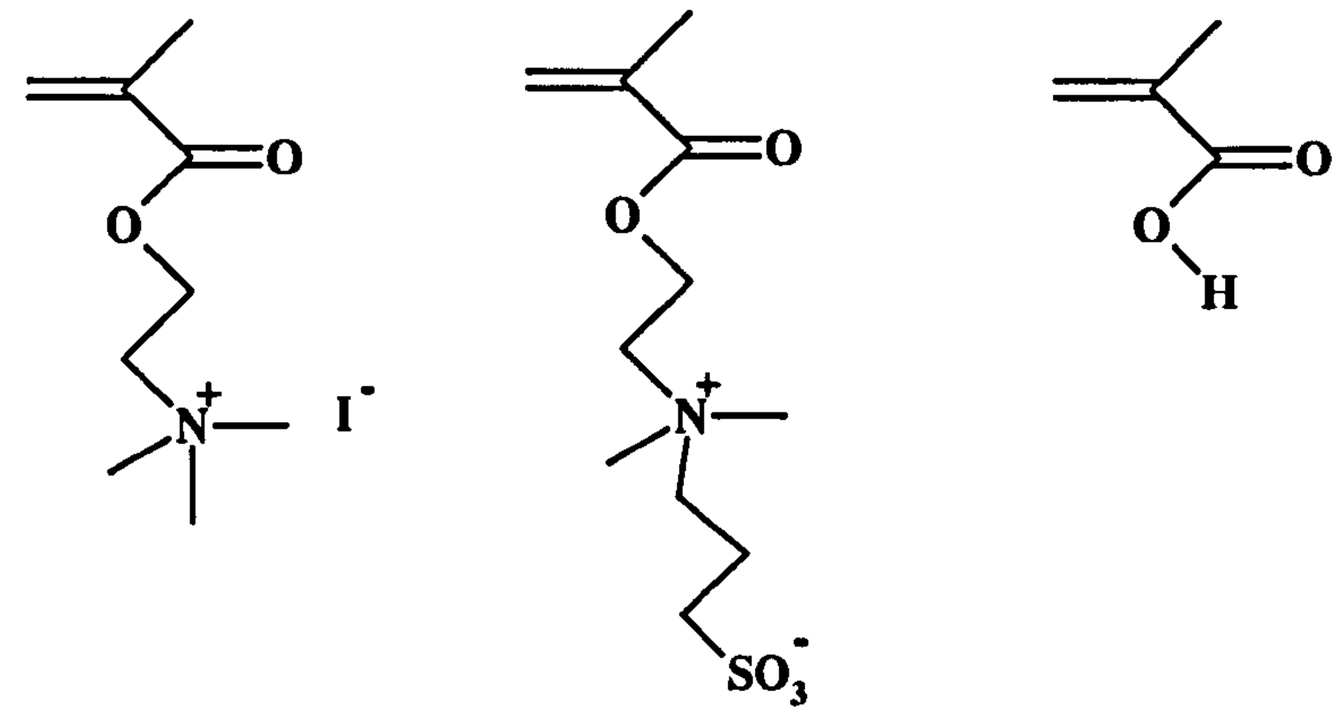
Figure 1.26 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (1.15) and 2-(Diethylamino)ethyl methacrylate (DEAEMA) (1.16)



DMAEMA (**1.15**) DEAEMA (**1.16**)

DMAEMA is a relatively cheap and commercially available monomer that is used in numerous home and personal care formulations. DMAEMA can be easily converted into its quaternary ammonium salt to incorporate hydrophilic character [16,64]. It is the aim of this research project to investigate controlled synthetic routes for the preparation of block and random co-polymers containing DMAEMA and/or DEAEMA and hydrophilic co-monomers. The hydrophilic co-monomers that have been investigated include several different quaternary ammonium salts of DMAEMA including the cationic monomer [2-(methacryloyloxy)ethyl]trimethylammonium iodide (DMAEMA.MeI) (**1.17**), the zwitterionic monomer 2-(dimethylamino)ethyl methacrylate, 1,3-propane sultone salt. [DMAEMA.1,3-PS] (**1.18**) and the anionic monomer methacrylic acid (MAA) (**1.19**).

Figure 1.27 Hydrophilic monomers



DMAEMA.MeI (1.17) DMAEMA.1,3-PS (1.18) MAA (1.19)

A series of tests have been performed to determine the dye-binding ability for the synthetic polymers prepared in this research. Tests have been designed to determine the dye-binding ability of these polymers under both laboratory conditions and simulated laundering.

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Chapter 2

SYNTHESIS & FUNCTIONALISATION OF HOMOPOLYMERS FROM FREE-RADICAL POLYMERISATION

Discovery consists of

looking at the same thing

as everyone else

and thinking

something different.

Albert Szert-Györgi

2.0 INTRODUCTION

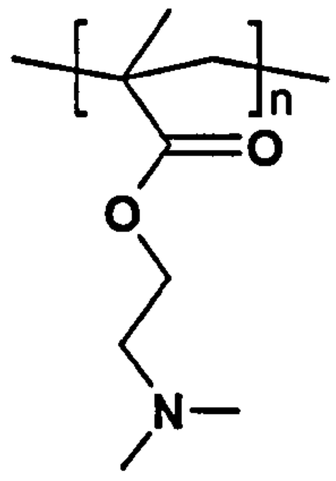
All current commercially available anti-dye transfer agents are based on homopolymers of PVP (**1.4**) and PVI (**1.5**) or their copolymer derivatives [1-4]. These systems are susceptible to precipitation when the polymer species becomes saturated with dye. The incorporation of anionic hydrophilic groups that improve solubility properties has been shown to dramatically reduce the dye-binding ability of the polymer [5].

This chapter will outline the synthesis of a series of PDMAEMA homopolymers from conventional free-radical polymerisation techniques and their functionalisation to produce a series of statistically quaternised and betainised PDMAEMA co-polymers. This method has been used to synthesise a variety of different co-polymer species containing different percentages of hydrophilic cationic monomer with respect to DMAEMA.

The PDMAEMA homopolymer species have been analysed for their dye binding ability. The dye binding constants for a variety of functional PDMAEMA co-polymers with Direct Red 80 (**1.1**) have been investigated to determine how the incorporation of statistical cationic hydrophilic functionality affects the dye binding constant.

2.1 RESULTS AND DISCUSSION

2.1.1 Synthesis of PDMAEMA homopolymer (2.1)



PDMAEMA (**2.1**)

A series of PDMAEMA homopolymers were synthesised by solution polymerisation in THF at 70 °C for 72 hours. The average molecular weight of the polymer obtained was adjusted by altering the weight percentage of initiator used (AIBN) with respect to the monomer. This is in accordance with the known relationship that molecular weight is inversely proportional to the square route of the initiator concentration. Table 2.0 lists the weight percentage of initiator used for each polymerisation together with the reaction composition.

Table 2.0 Reaction composition for polymerisation of DMAEMA (2.1)

AIBN (wt %)	AIBN (g)	DMAEMA (g)	THF (ml)
0.5	0.25	50	94
0.1	0.05	50	94
0.01	0.025	50	94

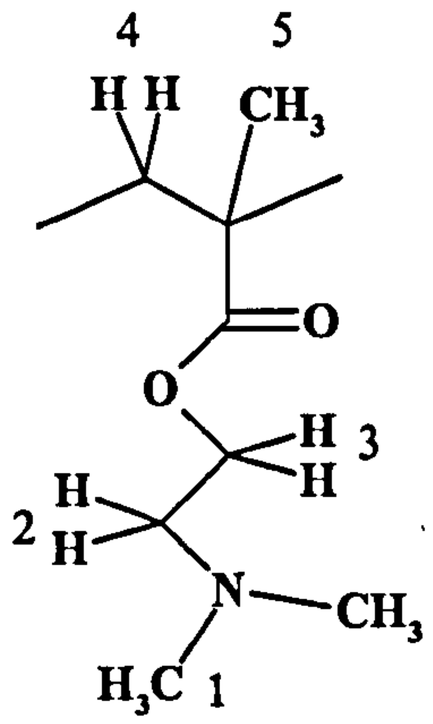
Table 2.1 lists the molecular weight data for the products obtained. The molecular weight distribution of the products was determined by GPC analysis. The conversions for all reactions were determined by gravimetry (oven drying to constant mass).

Table 2.1 Molecular weight and conversion analyses for the free-radical polymerisation products of DMAEMA (2.1)

AIBN (wt %)	Mn	PDi	Conversion (%)
0.5	22 400	3.16	99.9
0.1	44 700	2.41	97.7
0.01	55 700	2.30	93.2

The ^{1}H NMR for the PDMAEMA (**2.1**) product (Mn = 22 400) from reaction with 0.5% AIBN is given in Figure 2.1.

Figure 2.1 250 MHz, ^{1}H NMR in $CDCl_3$ of PDMAEMA (2.1)



PDMAEMA (**2.1**)

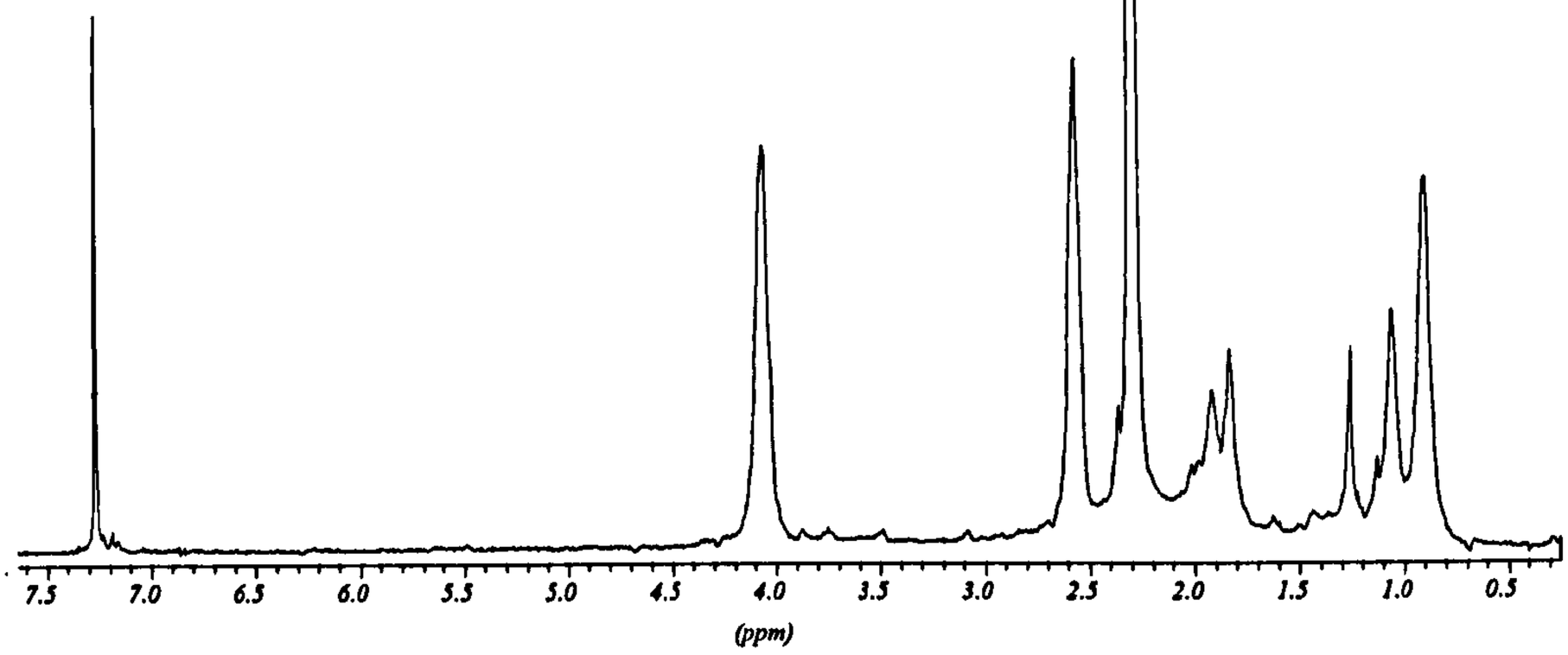


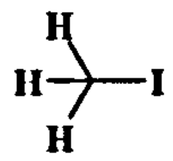
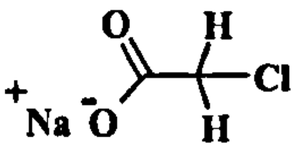
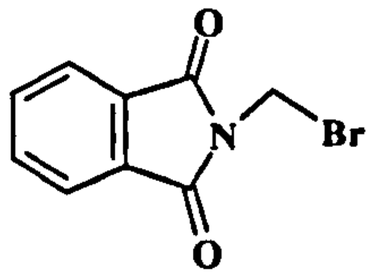
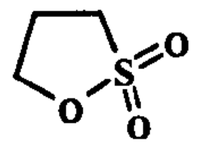
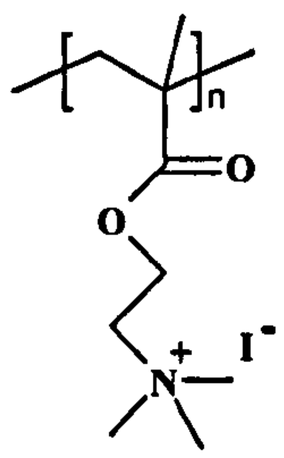
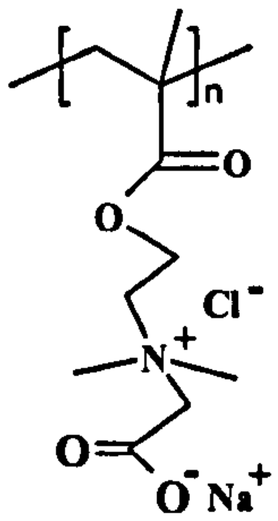
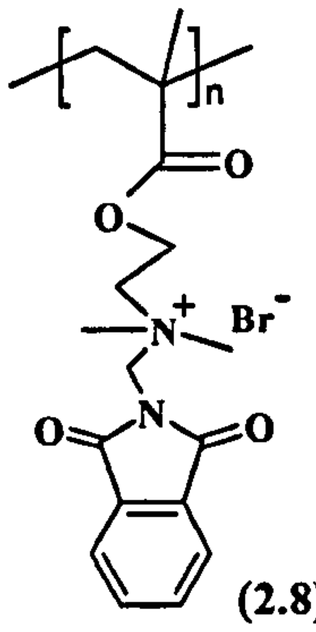
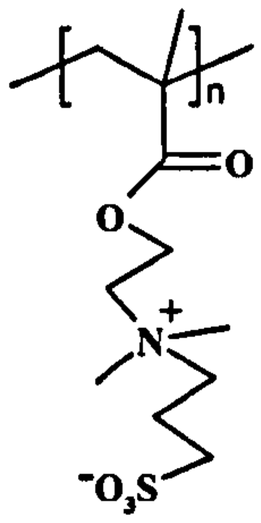
Table 2.2 Peak Assignment for the 250 MHz, ^{1}H NMR spectrum in $CDCl_3$ of the PDMAEMA (2.1)

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
7.27	Singlet	-	$CDCl_3$
4.06	Broad Singlet	2.00	H^3
2.41	Broad Singlet	2.09	H^2
2.30	Broad Singlet	6.35	H^1
1.85	Broad Multiplet	1.82	H^5
0.84	Broad Multiplet	2.85	H^4

The assignment from the NMR shows that the homopolymer that is formed is pure and that no residual monomer is present.

The introduction of a controlled degree of hydrophilic functionality was performed so as to determine the effect of incorporating statistical quaternary charge and zwittterionic charge on the dye binding ability of the homopolymer. The PDMAEMA (**2.1**) homopolymer (Mn = 22400) was reacted with a series of reagents to form the respective quaternary ammonium salts and betaines. Figure 2.2 lists the different types of reagents that have been used and the products that have been formed from their equimolar reaction with respect to the amine residue in the PDMAEMA (**2.1**) homopolymer. The reagents used were methyl iodide (**2.2**) [6,7], sodium chloroacetate (**2.3**), n-bromomethyl phthalimide (**2.4**) and 1,3-propane sultone (**2.5**) [8-11]. These reagents provide a suitable variety to determine how different functionalities affect the dye-binding ability of the polymer.

Figure 2.2 Quaternisation reagents used to form the quaternary ammonium salt complexes of PDMAEMA (2.1)

Quaternisation Reagent	 methyl iodide **(2.2)**	 chloroacetic acid, sodium salt **(2.3)**	 n-bromomethyl pthalimide **(2.4)**	 1,3-propane sultone **(2.5)**
homopolymer products from reaction with PDMAEMA (2.1)	 **(2.6)**	 **(2.7)**	 **(2.8)**	 **(2.9)**

2.1.2 Quaternisation of PDMAEMA (2.1) homopolymer (Mn 22 400) with methyl iodide (2.3)

A series of quaternisation reactions were performed for PDMAEMA (**2.1**) homopolymer (Mn = 22400) with methyl iodide. The reactions were performed to produce products with a range of degrees of quaternisation based on the concentration of the amine groups in the homopolymer. PDMAEMA homopolymer (2 g) and methyl iodide were reacted in THF solution and stirred at room temperature for 24 hours. Table 2.3 lists the composition for each reaction performed.

Table 2.3 Reagent composition for quaternisation of PDMAEMA (2.1) (Mn = 22400) with methyl iodide

Desired Quaternisation (%)	$RN(Me)_2$ groups in 2 g PDMAEMA (mol) x 10^{-2}	MeI (mol) x 10^{-4}	MeI (g) x 10^{-2}	THF (ml)
1	1.27	1.27	1.81	70
5	1.27	6.35	9.05	70
10	1.27	12.7	18.1	70
20	1.27	25.4	36.2	70
40	1.27	50.8	72.4	70
100	1.27	127	181	70

After 24 hours the products from reactions containing greater than 20% methyl iodide with respect to the amine residue had precipitated from solution. All of the other reactions remained homogeneous.

The degree of quaternisation obtained for each reaction was determined by the analysis of the product polymer by ^1H NMR spectroscopy in D_2O. The ^1H NMR spectrum for the product with 40% methyl iodide with respect to amine units is given in Figure 2.3

Figure 2.3 **250 MHz, ^1H NMR in D_2O of PDMAEMA statistical quaternary ammonium salt (2.10) preparec with 40% methyl iodide**

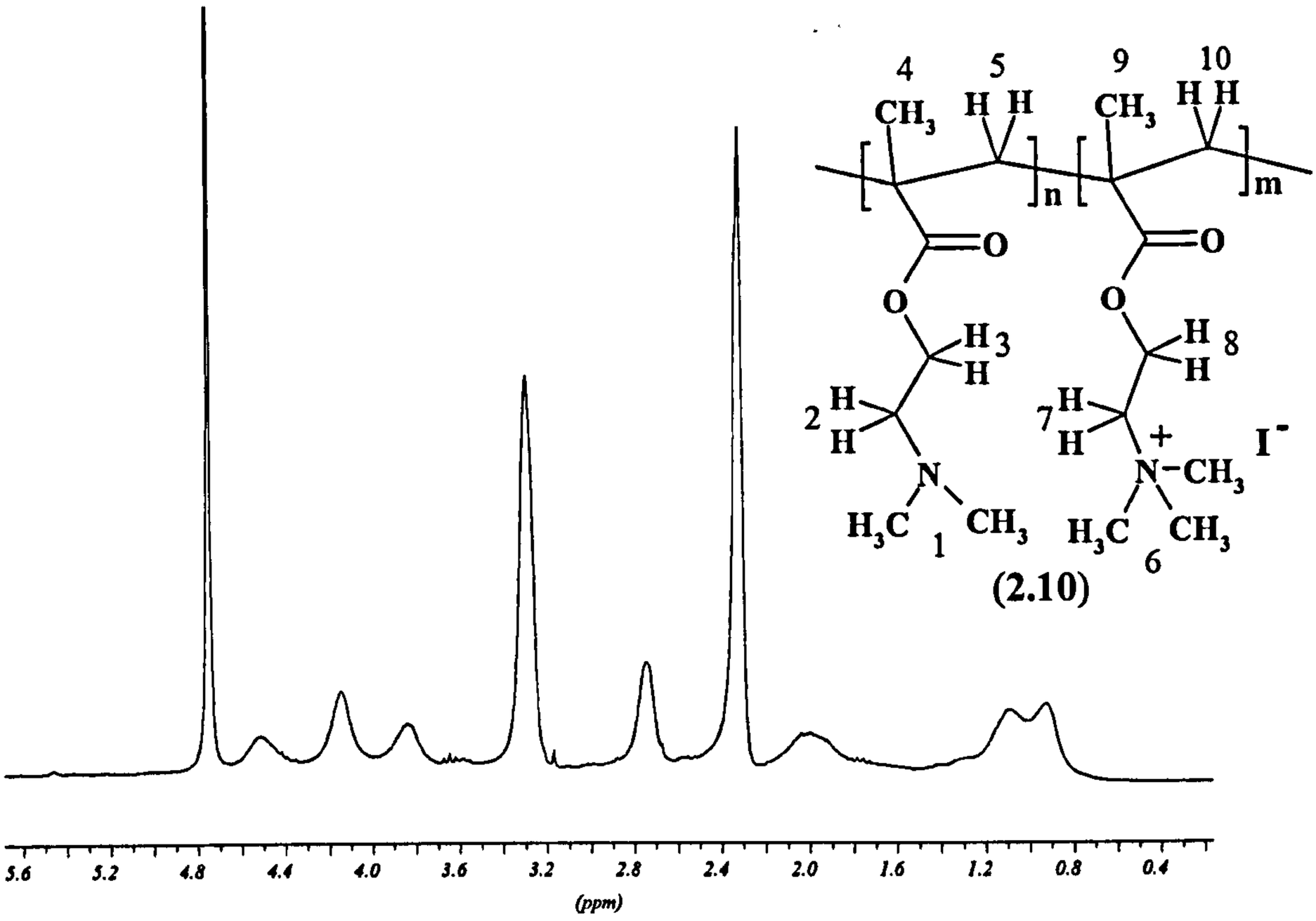


Table 2.4 **Peak Assignment for the 250 MHz, ^1H NMR spectrum in $CDCl_3$ of the PDMAEMA statistical quaternary ammonium salt (2.10) prepared with 40% methyl iodide**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
4.71	Singlet	-	D_2O
4.10	Broad Singlet	1.00	H^8
3.99	Broad Singlet	2.00	H^3
3.79	Broad Singlet	1.10	H^7
3.24	Broad Singlet	7.04	H^6
2.83	Broad Singlet	2.56	H^2
2.35	Broad Singlet	8.24	H^1
1.95	Broad Singlet	2.41	H^5,H^{10}
0.87	Broad Multiplet	5.03	H^4,H^9

The degree of quaternisation achieved for each sample is calculated based on the number of the tertiary amine groups with respect to the number of the quaternary amine groups found in the NMR. This is determined by taking the relative integral for one proton from H^{10} with respect to one proton from H^{6}.

$$\% \text{ quaternisation} = \frac{H^6/9}{(H^6/9 + H^1/6))} \times 100 = \frac{7.04/9}{7.04/9 + 8.24/6} \times 100 = 36.3\%$$

The ^1H NMR spectra of each product was recorded and from these data the percentage degree of quaternisation was calculated. Table 2.5 lists the percentage degree of quaternisation obtained for each reaction.

Table 2.5 Degree of quaternisation incorporated into PDMAEMA statistical quaternary ammonium salt (2.10) with methyl iodide

Percentage molarity of MeI added with respect to the amine residue (%)	Actual degree of quaternisation. Calculated from NMR analysis (%)
1	1.1
5	5.8
10	9.6
20	22.3
40	36.3
100	100

The data show that effective quaternisation is achieved for reaction of methyl iodide with PDMAEMA homopolymer (**2.1**).

2.1.3 Quaternisation of PDMAEMA (2.1) homopolymer (Mn 22400) with sodium chloroacetate (2.3)

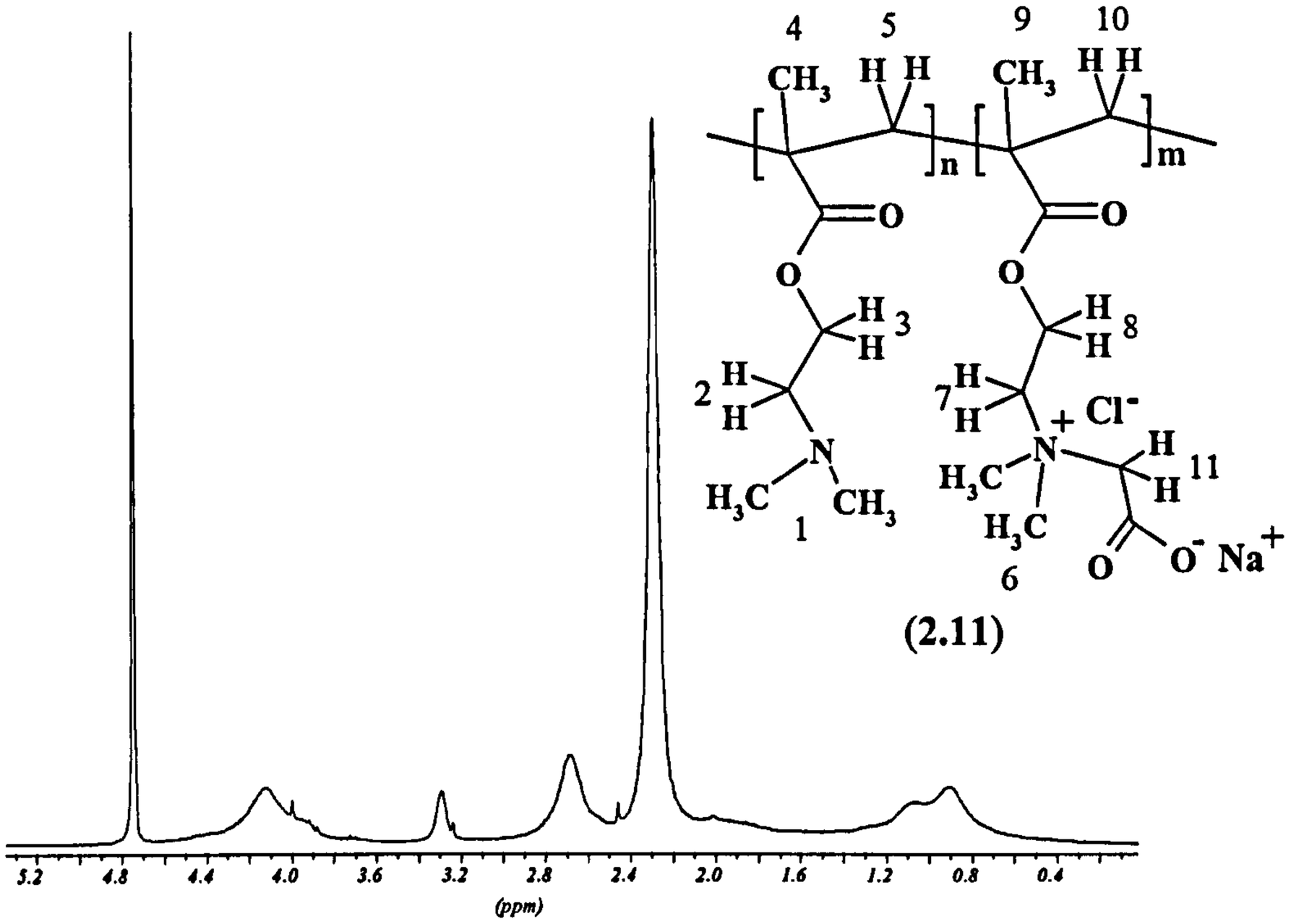
A series of quaternisation reactions were performed for PDMAEMA (**2.1**) homopolymer (Mn = 22400) with sodium chloroacetate. The reactions were performed to produce products with a range of degrees of quaternisation based on the concentration of the amine groups in the homopolymer. PDMAEMA homopolymer (2 g) and sodium chloroacetate were reacted in 50:50 Methanol:Water solution and stirred at room temperature for 24 hours. Table 2.6 lists the composition for each reaction performed.

Table 2.6 Reagent composition for quaternisation of PDMAEMA (2.1) (Mn = 22 400) with sodium chloroacetate

Desired Quaternisation (%)	$RN(Me)_2$ groups in 2 g PDMAEMA (mol) x 10^{-2}	Sodium chloroacetate (mol) x 10^{-4}	Sodium chloroacetate (g) x 10^{-2}	MeOH :H_2O 50:50 (ml)
1	1.27	1.27	1.48	80
5	1.27	6.35	7.41	80
10	1.27	12.7	14.8	80
20	1.27	25.4	29.6	80
40	1.27	50.8	59.3	80
100	1.27	127	148	80

The ^1H NMR spectrum for the product with 10% sodium chloroacetate with respect to amine units is given in Figure 2.4

Figure 2.4 **250 MHz, ^{1}H NMR in D_2O of PDMAEMA statistical quaternary ammonium salt (2.11) prepared with 10% sodium chloroacetate**



(2.11)

Table 2.7 **Peak Assignment for the 250 MHz, ^{1}H NMR spectrum in D_2O of the statistical quaternary ammonium salt (2.11) prepared with 10% sodium chloroacetate**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
4.71	Singlet	-	D_2O
4.13	Broad Multiplet	1.00	H^8, H^3, H^7, H^{11}
3.29	Singlet	0.31	H^6
2.68	Broad Singlet	0.93	H^2
2.29	Broad Singlet	4.14	H^1
1.88	Broad Singlet	0.32	H^5, H^{10}
0.92	Broad Multiplet	1.30	H^4, H^9

The degree of quaternisation obtained for each reaction was determined by the analysis of the product polymer by ^1H NMR spectroscopy in D_2O. The calculation is analogous to that performed in section 2.1.2 for the calculation of the degree of quaternisation for the methyl iodide quaternary ammonium salt.

Table 2.8 Degree of quaternisation incorporated into PDMAEMA statistical quaternary ammonium salt (2.11) with sodium chloroacetate, sodium salt

Percentage molarity of sodium chloroacetate added with respect to the amine residue (%)	Actual degree of quaternisation. Calculated from NMR analysis (%)
1	1.0
5	5.0
10	7.0
20	16.2
40	25.0
100	61.9

The data show that quaternisation of the PDMAEMA homopolymer (**2.1**) (Mn = 22400) with sodium chloroacetate was successful. The reaction is however less facile than the equivalent reaction with methyl iodide as seen by the decrease in the degree of quaternisation with increasing loading. The ability of the leaving group from the alkyl halide and the degree of steric hindrance at the nitrogen centre and the halide centre affect the rate of quaternisation of the tertiary amine. The order of leaving group ability is $I^- > Br^- > Cl^-$, where the iodide ion is the best leaving group. The reaction of the sodium chloroacetate is therefore limited due to the poor leaving group ability of the chloride ion and the relative increase in steric bulk at the halide centre in comparison with methyl iodide. This reduction in comparative reactivity is also observed in section 2.1.4 for the quaternisation reaction with n-bromomethyl phthalimide.

2.1.4 Quaternisation of PDMAEMA (2.1) homopolymer (Mn 22400) with n-bromomethyl phthalimide (2.4)

A series of quaternisation reactions were performed for PDMAEMA (**2.1**) homopolymer (Mn = 22400) with n-bromomethyl phthalimide. The reactions were performed to produce products with a range of quaternisation based on the concentration of the amine groups in the homopolymer. PDMAEMA homopolymer (2 g) and n-bromomethyl phthalimide were reacted in THF solution and stirred at room temperature for 24 hours. Table 2.9 lists the composition for each reaction performed.

Table 2.9 Reagent composition for quaternisation of PDMAEMA (2.1) (Mn = 22400) with n-bromomethyl phthalimide

Desired Quaternisation (%)	$RN(Me)_2$ groups in 2 g PDMAEMA (mol) x 10^{-2}	n-bromomethyl phthalimide (mol) x 10^{-4}	n-bromomethyl phthalimide (g) x 10^{-2}	THF (ml)
1	1.27	1.27	3.05	70
5	1.27	6.35	15.3	70
10	1.27	12.7	30.5	70
20	1.27	25.4	61.1	70
40	1.27	50.8	122	70
100	1.27	127	305	70

After 24 hours the reactions containing greater than 20% n-bromomethyl phthalimide with respect to the amine residue had precipitated. All other reactions remained homogeneous.

The ^1H NMR spectrum for the product with 10% n-bromomethyl phthalimide with respect to amine units is given in Figure 2.5

Figure 2.5 **250 MHz, ^{1}H NMR in D_2O of PDMAEMA statistical quaternary ammonium salt (2.12) prepared with 10% n-bromomethyl phthalimide**

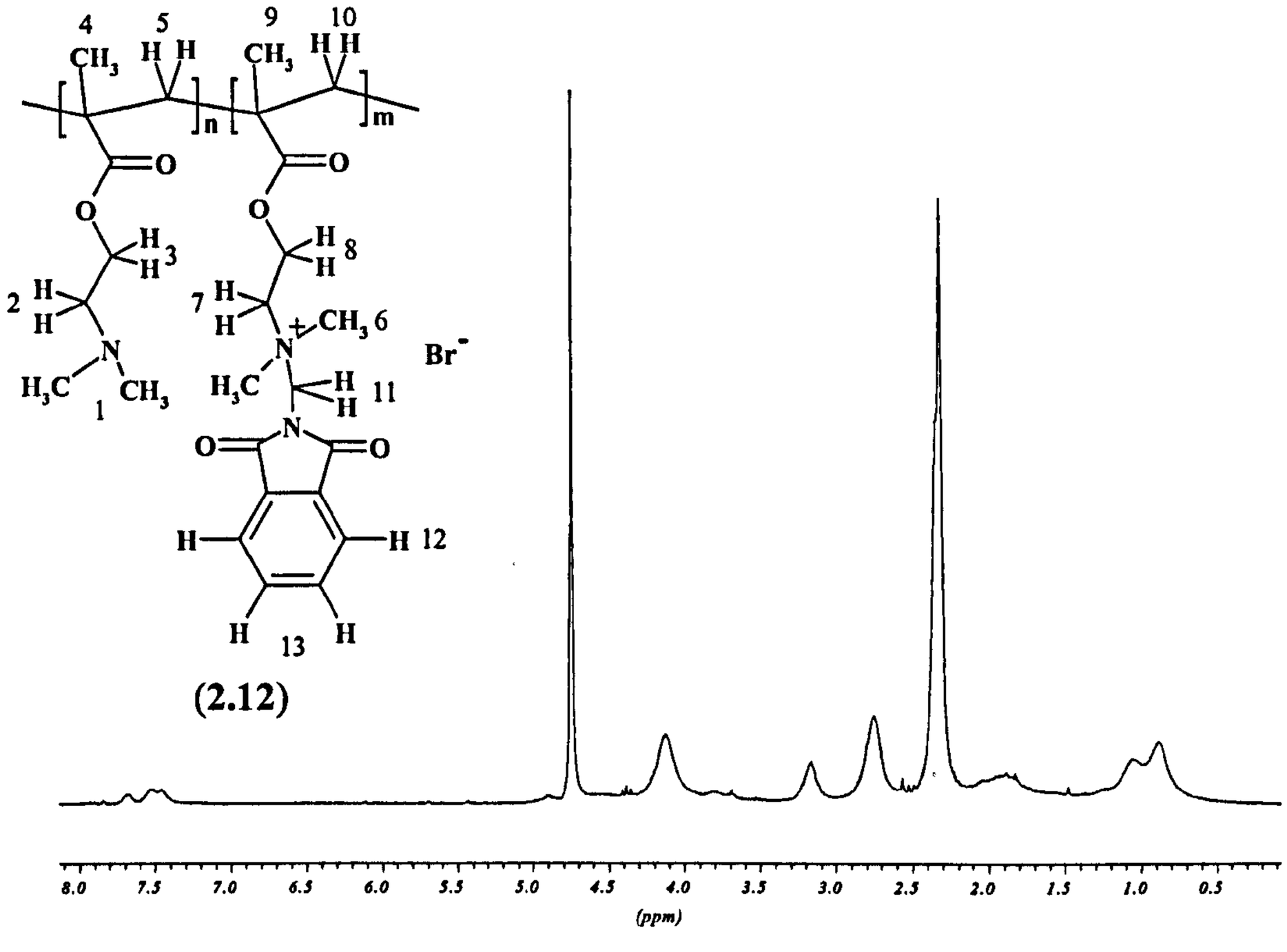


Table 2.10 **Peak Assignment for the 250 MHz, ^{1}H NMR spectrum in D_2O of PDMAEMA statistical quaternary ammonium salt (2.12) prepared with 10% n-bromomethyl phthalimide**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
7.52	Broad Multiplet	0.84	H^{12}, H^{13}
4.71	Singlet	-	D_2O
4.13	Broad Singlet	2.22	H^8, H^3, H^7, H^{11}
3.12	Broad Singlet	1.00	H^6
2.75	Broad Singlet	2.69	H^2
2.32	Broad Singlet	10.78	H^1
1.83	Broad Singlet	1.07	H^5, H^{10}
0.89	Broad Multiplet	4.13	H^4, H^9

The ^{1}H nmr spectra of the PDMAEMA statistical quaternary ammonium salt (**2.12**) with 10% n-bromomethyl phthalimide shows the presence of the protons on the phthalimide ring and a clear peak at δ 3.2 that is assigned as the two methyl groups attached to the quaternary nitrogen. The degree of quaternisation obtained for each reaction was determined by the analysis of the product polymer by ^{1}H NMR spectroscopy in D_2O. The calculation is analogous to that performed in section 2.1.2 for the calculation of the degree of quaternisation for the methyl iodide quaternary ammonium salt.

Table 2.11 Degree of quaternisation incorporated into PDMAEMA statistical quaternary ammonium salt (2.12) with n-bromomethyl phthalimide

Percentage molarity of n-bromomethyl phthalimide added with respect to the amine residue (%)	Actual degree of quaternisation. Calculated from NMR analysis (%)
1	1.4
5	4.9
10	8.5
20	15.3
40	33.2
100	100

The data show that quaternisation of the PDMAEMA homopolymer (**2.1**) (Mn = 22400) with n-bromomethyl phthalimide was again successful.

2.1.5 Quaternisation of PDMAEMA (2.1) homopolymer (Mn 22400) with 1,3-propane sultone (2.5)

A series of betainisation reactions were performed for PDMAEMA (**2.1**) homopolymer (Mn = 22400) with 1,3-propane sultone. The reactions were performed to produce products with a range of betainisation based on the concentration of the amine groups in the homopolymer. PDMAEMA homopolymer (2 g) and 1,3-propane sultone were reacted in THF solution and stirred at room temperature for 24 hours. Table 2.12 lists the composition for each reaction performed.

Table 2.12 Reagent composition for betainisation of PDMAEMA (2.1) (Mn = 22400) with 1,3-propane sultone

Desired Quaternisation (%)	$RN(Me)_2$ groups in 2 g PDMAEMA (mol) x 10^{-2}	1,3-propane sultone (mol) x 10^{-4}	1,3-propane sultone (g) x 10^{-2}	THF (ml)
1	1.27	1.27	1.55	70
5	1.27	6.35	7.77	70
10	1.27	12.7	15.5	70
20	1.27	25.4	31.1	70
40	1.27	50.8	62.2	70
100	1.27	127	155	70

After 24 hours the reactions containing greater than 20% 1,3-propane sultone with respect to the amine residue had formed precipitated product. All other reactions remained homogeneous.

The ^{1}H NMR spectrum for the product with 20% 1,3-propane sultone with respect to amine units is given in Figure 2.6

Figure 2.6 **250 MHz, ^{1}H NMR in D_2O of PDMAEMA statistical betaine (2.13) prepared with 20% 1,3-propane sultone**

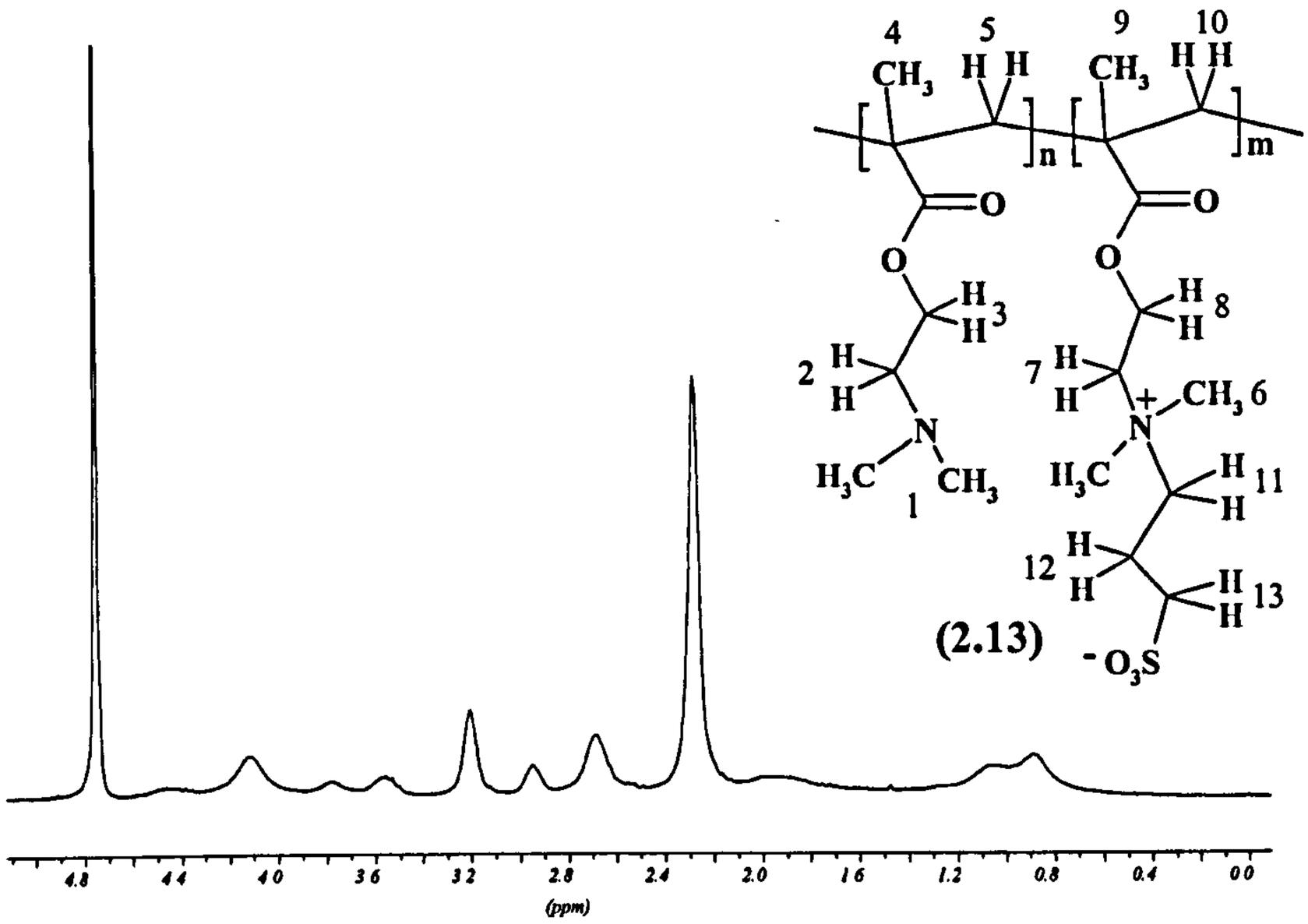


Table 2.13 **Peak Assignment for the 250 MHz, ^{1}H NMR spectrum D_2O of PDMAEMA statistical betaine (2.13) prepared with 20% 1,3-propane sultone**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
4.71	Singlet	-	D_2O
4.41	Broad Singlet	0.50	H^8
4.11	Broad Singlet	2.63	H^3
3.75	Broad Singlet	0.53	H^7, H^{11}
3.56	Broad Singlet	0.92	H^{13}
3.20	Broad Singlet	3.08	H^{12}
2.95	Broad Singlet	1.00	H^6
2.69	Broad Singlet	2.68	H^2
2.28	Broad Singlet	13.92	H^1
1.94	Broad Singlet	1.11	H^5, H^{10}
0.89	Broad Multiplet	5.68	H^4, H^9

The ^1H nmr spectra of the PDMAEMA statistical betaine (**2.13**) with 20% 1,3-propane sultone shows the incorporation of the 1,3-propane sultone [11]. The degree of betainisation obtained for each reaction was determined by the analysis of the product polymer by ^1H NMR spectroscopy in D_2O. The calculation is analogous to that performed in section 2.1.2 for the calculation of the degree of quaternisation for the methyl iodide quaternary ammonium salt.

Table 2.14 Degree of quaternisation incorporated into PDMAEMA statistical quaternary ammonium salt (2.13) with 1,3-propane sultone

Percentage molarity of 1,3-propane sultone added with respect to the amine residue (%)	Actual degree of quaternisation. Calculated from NMR analysis (%)
1	2.0
5	7.1
10	11.0
20	18.1
40	34.6
100	100

The data show that betainisation of the PDMAEMA homopolymer (**2.1**) (Mn = 22400) with 1,3-propane sultone was successful. The degree of quaternisation obtained for the reaction where 5% quaternisation was expected gave 7.1% quaternisation this is an error incurred due to lack of accuracy in weighing out the liquid 1,3-propane sultone reagent.

2.2 CONCLUSIONS

A selection of PDMAEMA homopolymers have been successfully synthesised. The PDMAEMA homopolymer (**2.1**) (Mn = 22400) has been functionalised to produce a series of new statistical co-polymer species and homopolymers containing quaternary ammonium salts and betaines. All of the polymers produced have been analysed to determine their dye binding ability. The results of these tests are given in Chapter 7.

2.3 REFERENCES

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Chapter 3

CATALYTIC CHAIN-TRANSFER MEDIATED POLYMERISATION

If at first,

an idea is not absurd,

then there is no hope for it.

Albert Einstein

3.0 INTRODUCTION

Catalytic chain-transfer mediated polymerisation is an established method for obtaining reduction in the average molecular weight for a radical polymerisation [1-4]. The chemistry and the mechanism for catalytic chain-transfer (CCT) polymerisations were reviewed in Chapter 1, section 1.4.1.3. This chapter will study the application of CCT mediated polymerisation as a method for the preparation of low molecular weight functional macromonomers containing ω-terminal unsaturation [5-7].

Chapter 4 section 4.1 describes how macromonomers containing ω-terminal unsaturation can be used in co-polymerisation reactions for the preparation of block and graft co-polymer species. It is a primary target of this body of research to develop methods for the syntheses of block and graft co-polymer species that contain at least one monomer type that will provide hydrophilic functionality and one monomer type that will provide anti-dye transfer activity. CCT mediated polymerisation has been investigated as a possible method for the synthesis of functional macromonomers that exhibit either anti-dye transfer activity or that can provide hydrophilic functionality.

The monomer that is of interest for its use as anti-dye transfer agents is 2-(dimethylamino)ethyl methacrylate (DMAEMA). Hydrophilic monomers that are of interest include the cationic, quaternary ammonium salts of DMAEMA as well as the anionic hydrophilic monomer methacrylic acid (MAA).

3.1 RESULTS AND DISCUSSION

3.1.1 Chain-Transfer Agent

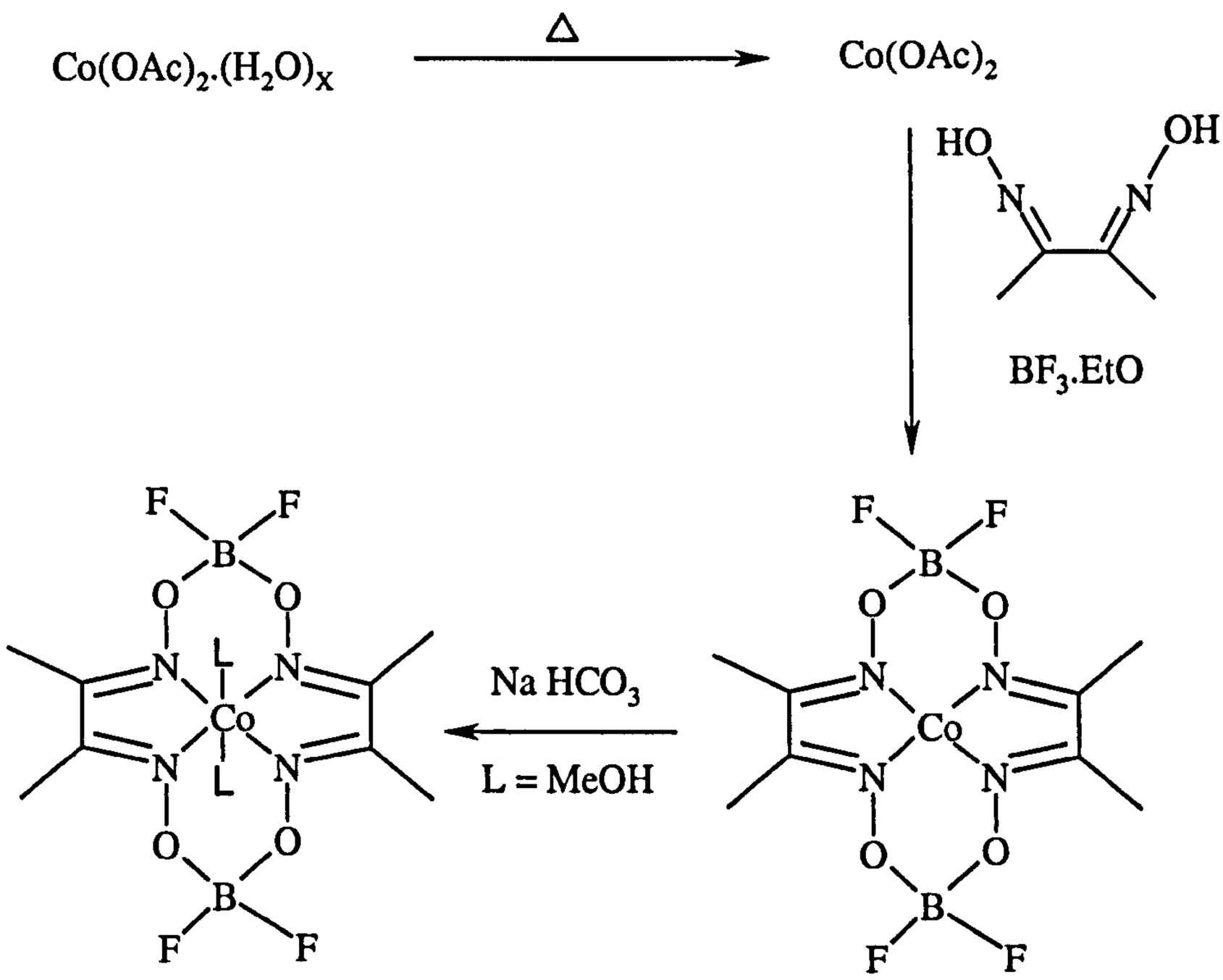
The catalytic chain-transfer agent that has been used for all of these studies is CoBF (**1.11**). CoBF is a low spin Co(II) macrocycle based upon a boron difluoride bridged cobaloxime. Previous authors have shown that CoBF has a

high chain-transfer constant with methacrylate monomers [8-11] and is hydrolytically stable compared with Co(II) analogues that do not contain BF_2 bridging [12], these factors have enabled CCT polymerisation to be used with a wide range of functional monomers and solvents, including aqueous based systems.

3.1.1.1 Synthesis and Characterisation of CoBF (1.11)

The catalytic chain-transfer agent CoBF **(1.11)** was prepared using a variation of the method of Bakac and Espenson [13,14] as described in the Experimental section. Figure 3.0 outlines the synthetic route.

Figure 3.0 Preparation of CoBF



CoBF (**1.11**) was obtained in high yield and was purified by recrystallisation from methanol. Analysis of the CoBF transfer agent by visible spectroscopy and elemental analysis showed that the recrystallised product was of high purity. Mass spectrometry of the product is not possible due to the low volatility of the catalyst and NMR studies of the catalyst are difficult since the Co(II) metal centre is low spin d^7 and is therefore paramagnetic.

Table 3.0 Visible spectrum and elemental analysis data for CoBF

	CHN analysis			**Visible data** (nm)
	H %	C %	N %	λ max
CoBF	26.72 (1)	4.48 (1)	12.41 (1)	460 (2)
CoBF (found)	26.63	4.41	12.25	448

(1) Data for calculated theoretical weight percentages of C, H and N for the methanol adduct of CoBF.

(2) Reference data quoting the λ max for a low spin Co(II) macrocycle derivative of CoBF [15].

3.1.2 Measurement of the chain transfer co-efficient, Cs of CoBF

The ability of a chain transfer agent to induce a molecular weight reduction in a polymerisation process is quantified by the chain-transfer co-efficient, Cs. The favoured method for the determination of the chain-transfer co-efficient, Cs is by using the Mayo equation (1.7) [16]. A derivation of the Mayo equation is given in section 1.5.1.1.

$$\frac{1}{D_P} = \frac{1}{D_{P0}} + Cs\frac{[T]}{[M]} \qquad (1.7)$$

Dp is the number average degree of polymerisation in the presence of the transfer agent. Dp_0 is the number average degree of polymerisation for an analogous reaction where no transfer agent is present. [T] and [M] are the respective concentrations of transfer agent and monomer. Cs is the chain-transfer co-efficient.

A series of polymerisations are performed under identical conditions to give a low conversion with a range of [T]:[M] ratios. One polymerisation is performed where no catalyst is added and four other reactions are performed with increasing [T]:[M] ratio. The Dp for each polymerisation is measured by GPC. Dp_0 is calculated for the sample where no catalyst is present. The value of Cs for each reaction containing transfer agent is obtained by manipulation of the Mayo equation.

A plot of $(1/Dp)-(1/Dp_0)$ versus [T]/[M] gives a straight-line that passes through the origin and with a gradient equal to the Cs. This type of graph is referred to as a Mayo plot. The value of Cs that is calculated from the gradient represents the mean Cs based on the scatter of data from all of the individual polymerisations performed [10,17].

3.1.2.1 Chain-Transfer Constant of CoBF for the polymerisation of MMA in bulk at 60 °C

The experimental conditions and the data from the GPC analysis of the product polymers are given in Table 3.1.

Table 3.1 Experimental data for the bulk polymerisation of MMA with CoBF

MMA (g)	AIBN (mg)	[CoBF]/[MMA] x10^{-7}, (Molar Ratio)	Mn	Pdi	Conv (%)
4.68	25	-	58100	2.20	4.9
4.68	25	0.93	19900	2.27	4.2
4.68	25	1.85	13100	2.07	4.0
4.68	25	3.70	12200	2.20	3.2
4.68	25	7.40	2700	2.26	2.9

Figure 3.1 Mayo Plot for Bulk Polymerisation of MMA With CoBF at 60°C

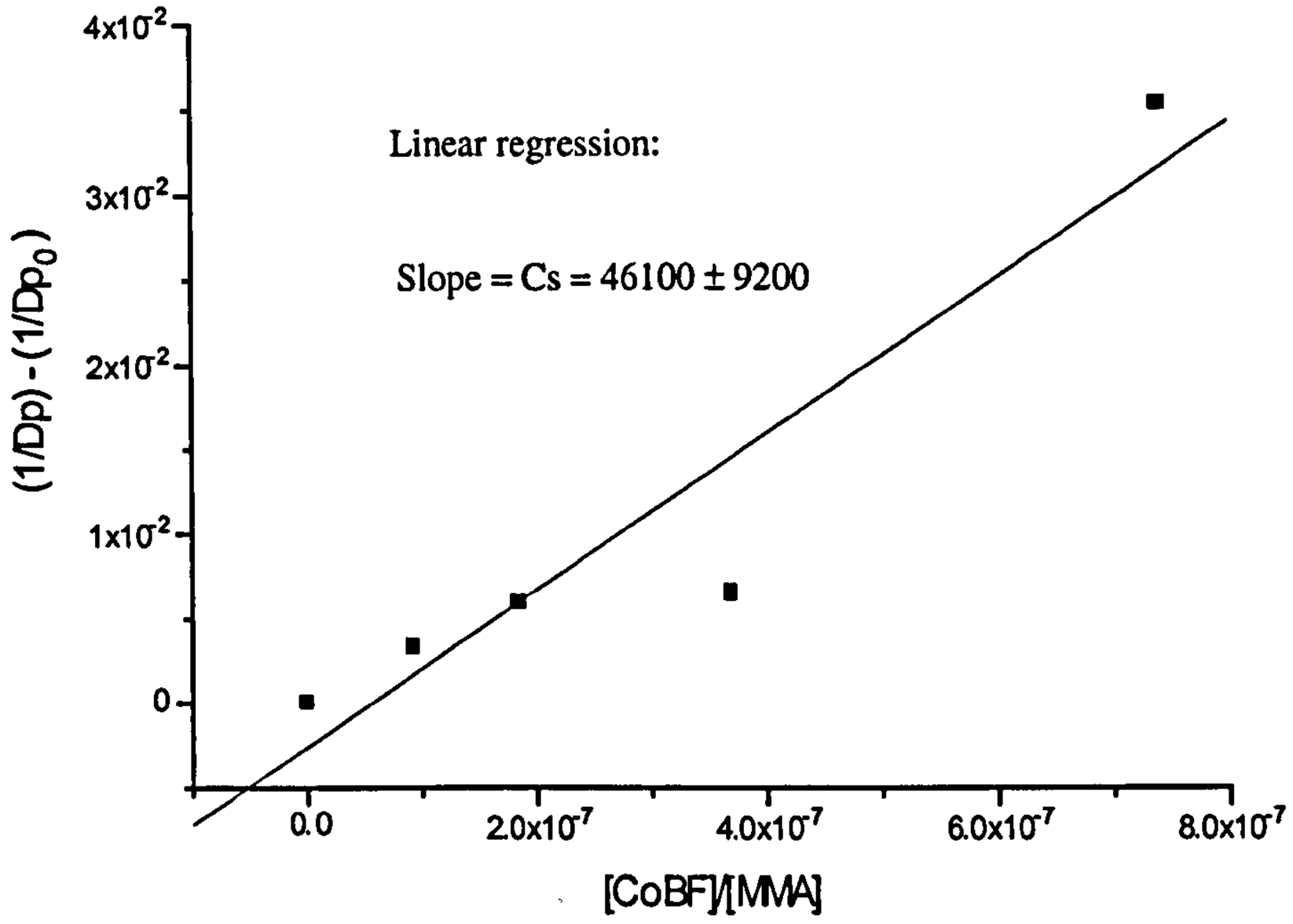


Table 3.2 Calculated Cs data for the bulk polymerisation of MMA with CoBF at 60°C

[CoBF]/[MMA] x10^{-7}	Dp	1/Dp x10^{-3}	(1/Dp)-(1/Dp_0) x10^{-3}	Cs (Calculated)
-	580.8	1.72	0	-
0.93	199.7	5.01	3.29	35500
1.85	131.3	7.62	5.90	31900
3.70	121.8	8.21	6.49	17500
7.40	27.0	37.05	35.33	47700
Mean Cs from calculations				33200
Cs from Mayo plot				46100

The calculated value of the Cs for CoBF in the bulk polymerisation of MMA at 60 °C is in good agreement with the literature values [8,18]. The Cs calculated from the gradient shows that one anomalous data point is present for the reaction where [CoBF]/[MMA] = 3.7x10^{-7}. The degree of scatter is low in comparison to the published data and the value for Cs as defined by the gradient agrees well with the individually calculated values. It should be noted that the conversion decreases with increasing [CoBF], this shows that CoBF inhibits the rate of the reaction.

3.1.2.2 Chain-Transfer Constant of CoBF for the polymerisation of DMAEMA in bulk at 60 °C

The Cs value of CoBF with the tertiary amine functional monomer DMAEMA was determined. During the preparation of the stock solution for the reaction where the ratio of [CoBF]/[MMA] was 75 x 10^{-7} it was observed that, as the repeated freeze/pump/thaw cycle was performed, a colour change from an orange solution through green to produce a clear dark blue solution occurred. All other reaction solutions remained orange in colour. The change in colour

that is observed for certain CCT mediated polymerisation of DMAEMA has been investigated and the results are given in section 3.1.4.

Table 3.3 Experimental data for the bulk polymerisation of DMAEMA with CoBF

[CoBF]/[DMAEMA] $x10^{-7}$ (Molar Ratio)	DMAEMA (ml)	AIBN (mg)	Mn (GPC)	PDi	Conv (%)
-	4.67	25	53100	3.22	15.1
9.38	4.67	25	39200	3.14	12.3
18.75	4.67	25	18300	2.75	9.3
37.51	4.67	25	11700	2.62	5.1
75.02	4.67	25	4200	2.34	6.4

Figure 3.2 Mayo Plot for Bulk Polymerisation of DMAEMA With CoBF at 60 °C

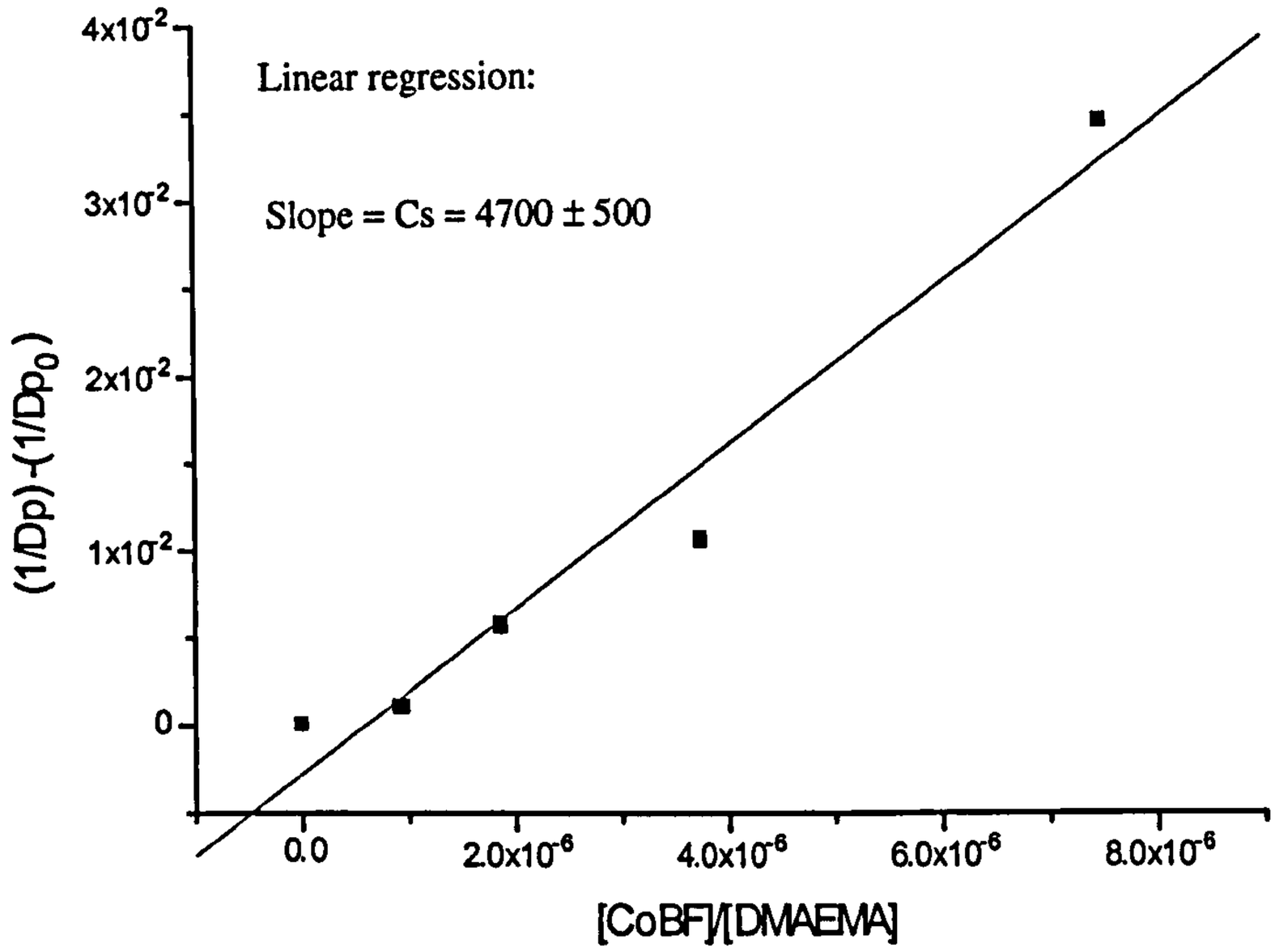


Table 3.4 Calculated Cs data for the bulk polymerisation of MMA with CoBF at 60 °C

[CoBF]/[MMA] x10^{-7}	Dp	1/Dp x10^{-3}	(1/Dp)-(1/Dp_0) x10^{-3}	Cs (Calculated)
-	337.7	2.96	0	-
9.38	249.2	4.01	1.05	1100
18.75	116.4	8.59	2.93	1600
37.51	74.5	13.42	10.46	2800
75.02	26.7	37.45	34.49	4600
Mean Cs from calculations				2500
Cs from Mayo plot				4700

The experimental data shows that molecular weight reduction is obtained, although the activity of the catalyst is significantly reduced in comparison to its activity with MMA. The Cs for the bulk polymerisation of DMAEMA with CoBF as determined in this study is much lower than that quoted in previous work, i.e., Cs of 4700 ± 500 compared with 27500 ± 38800 [19]. The high reproducibility of the data obtained in this study with different monomer batches together with the high degree of error quoted in the reference material suggests that the previously reported data is inaccurate [19].

3.1.3 The preparation of low molecular weight functional macromonomers from CCT mediated polymerisation with CoBF

The molecular weight data from the macromonomer products can be used to construct a pseudo-Mayo plot where a value of Cs for the particular preparative procedure can be calculated. This data can be used to calculate the desired amount of chain-transfer agent that is required to produce a specific molecular weight product.

3.1.3.1 The preparation of low molecular weight macromonomers from CCT mediated bulk polymerisation of DMAEMA

A series of experiments with different concentrations of [CoBF] with respect to [DMAEMA] were performed in bulk polymerisation at 70 °C. Table 3.5 lists a complete range of the PDMAEMA macromonomers that were prepared from bulk CCT polymerisation. The relative concentration of [CoBF] compared to [Monomer] is given as a value in terms of the amount of catalyst expressed in parts per million (ppm) with respect to monomer.

Table 3.5 Conversion and molecular weight data for DMAEMA macromonomers after 46 hours from bulk CCTP

CoBF (ppm)	Mn (46 hours) (GPC)	PDi	% Conversion (46 hours)
20	3400	2.10	48.8
30	3100	1.92	46.0
40	1200	1.69	33.7
50	900	1.58	21.0
80	540	1.31	12.6
100	430	1.14	10.7
150	430	1.14	8.8
375	400	1.14	7.2

The data for samples taken periodically from two of these bulk polymerisations of DMAEMA with CoBF (30ppm and 40ppm) are given in table 3.6.

Table 3.6 Conversion and molecular weight data for the bulk polymerisation of DMAEMA with 30 and 40 ppm CoBF

Reaction	Sample (hours)	Mn	PDi	Conversion (%)
30 ppm CoBF	24	2800	1.86	34.5
	46	3100	1.92	46.5
	72	4000	2.06	51.2
	96	5900	3.11	80.0
40 ppm CoBF	24	1170	1.58	13.7
	46	1170	1.69	16.1
	72	1190	1.54	16.7
	96	1100	1.70	18.1

Figure 3.3 Plot of Mn and PDi versus conversion for the bulk polymerisation of DMAEMA at 70 °C with 30 ppm CoBF

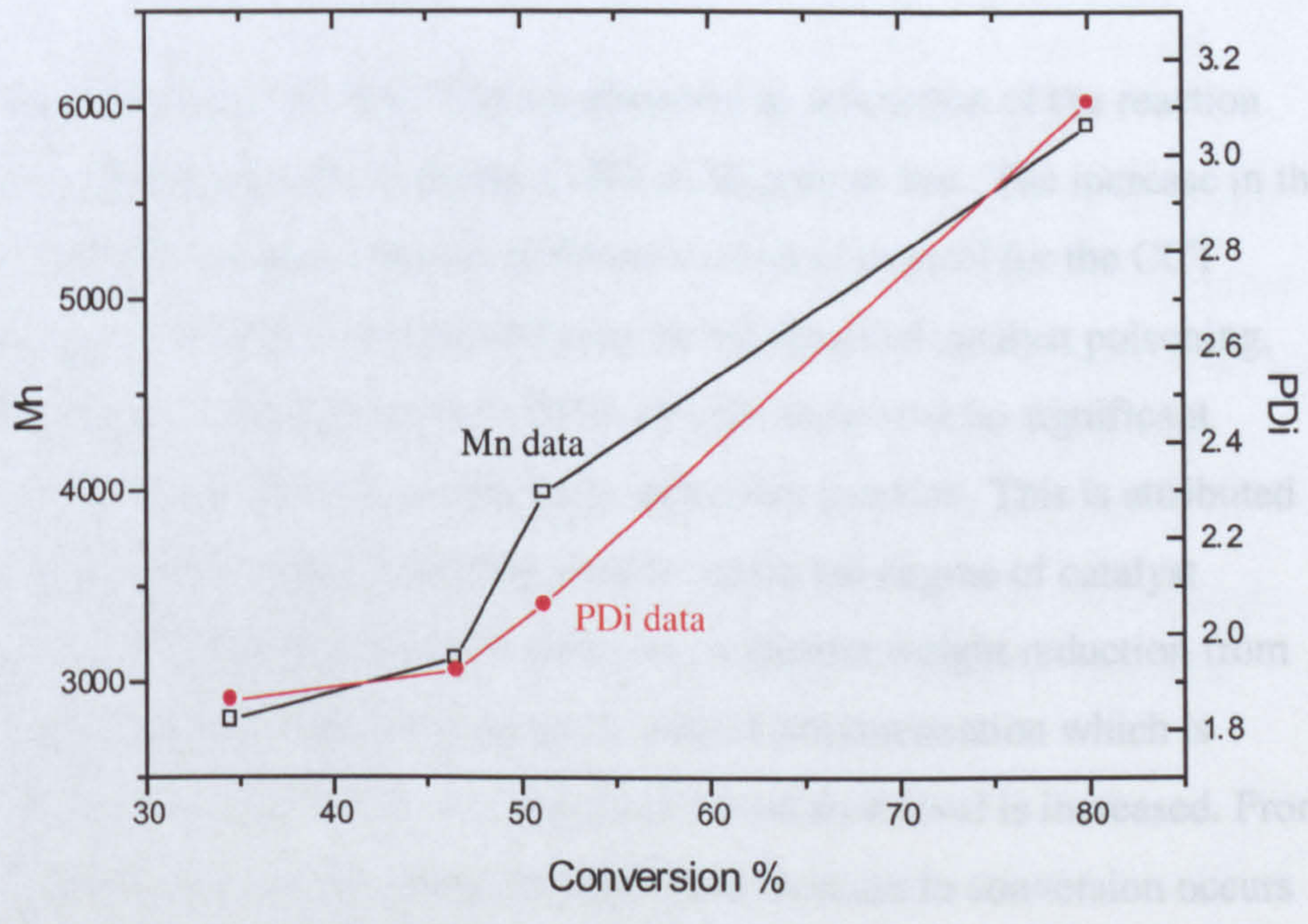
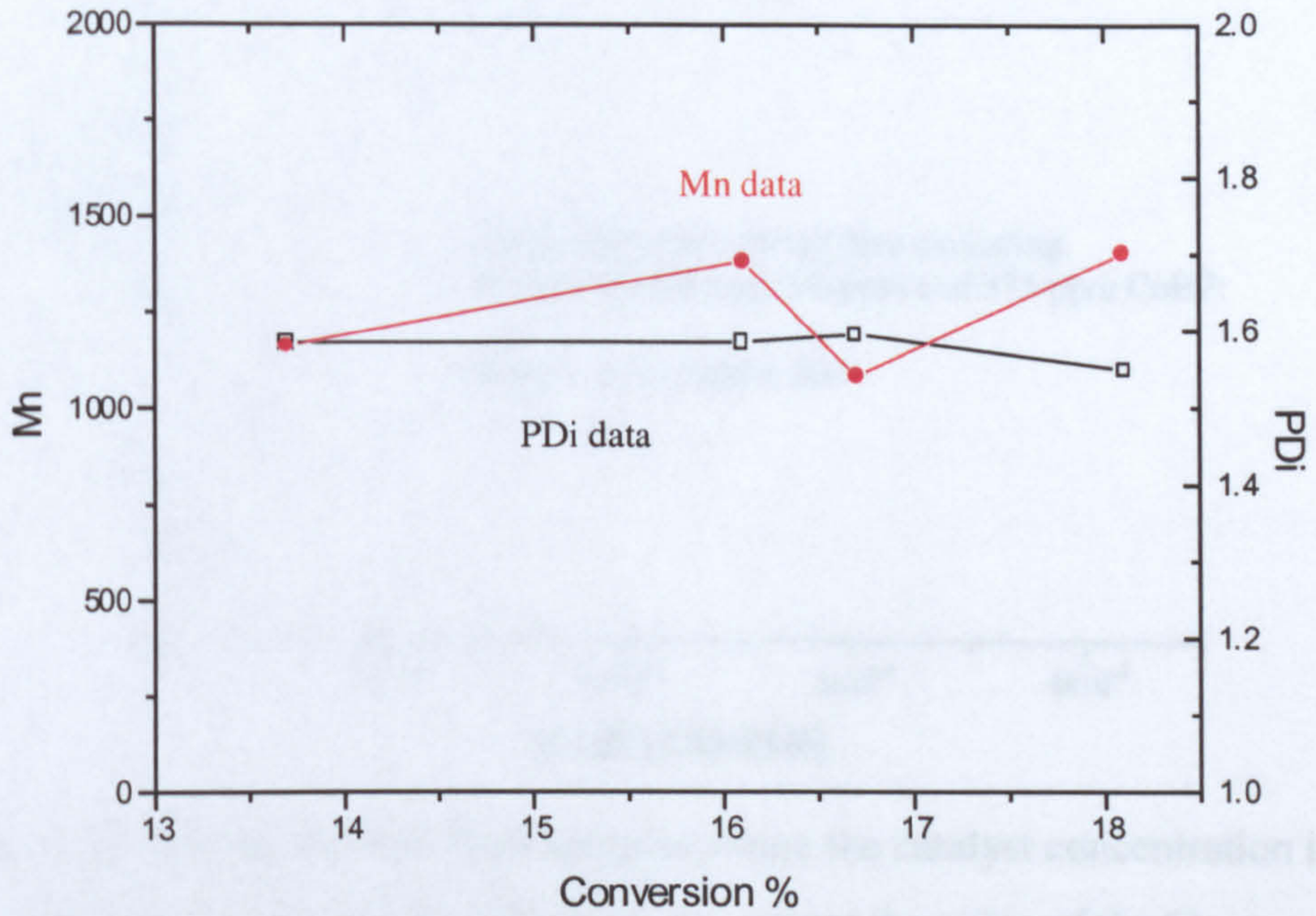


Figure 3.4 Plot of Mn and PDi versus conversion for the bulk polymerisation of DMAEMA at 70 °C with 40 ppm CoBF



An increase in the Mn and the PDi are observed as a function of the reaction time for polymerisations containing CoBF at 30 ppm or less. The increase in the Mn and the PDi for these samples represents a loss of control for the CCT mediated polymerisation process and may be the result of catalyst poisoning. Polymerisations conducted with CoBF > 30 ppm show that no significant change in the Mn or PDi occurs for each respective reaction. This is attributed to a threshold level of catalyst being present where the degree of catalyst poisoning is insufficient to prevent effective molecular weight reduction from occurring. The Co(II) catalyst reduces the rate of polymerisation which is observed as a lowering of the conversion as the catalyst level is increased. From the conversion data it is clear that no significant increase in conversion occurs after 46 hours. Thus all PDMAEMA macromonomers prepared from bulk polymerisations were terminated after 46 hours to reduce effects due to undesired termination reactions.

A pseudo Mayo plot of the data for the products obtained at 46 hours is given in figure 3.5.

Figure 3.5 Pseudo Mayo plot for bulk CCT of DMAEMA at 70°C.

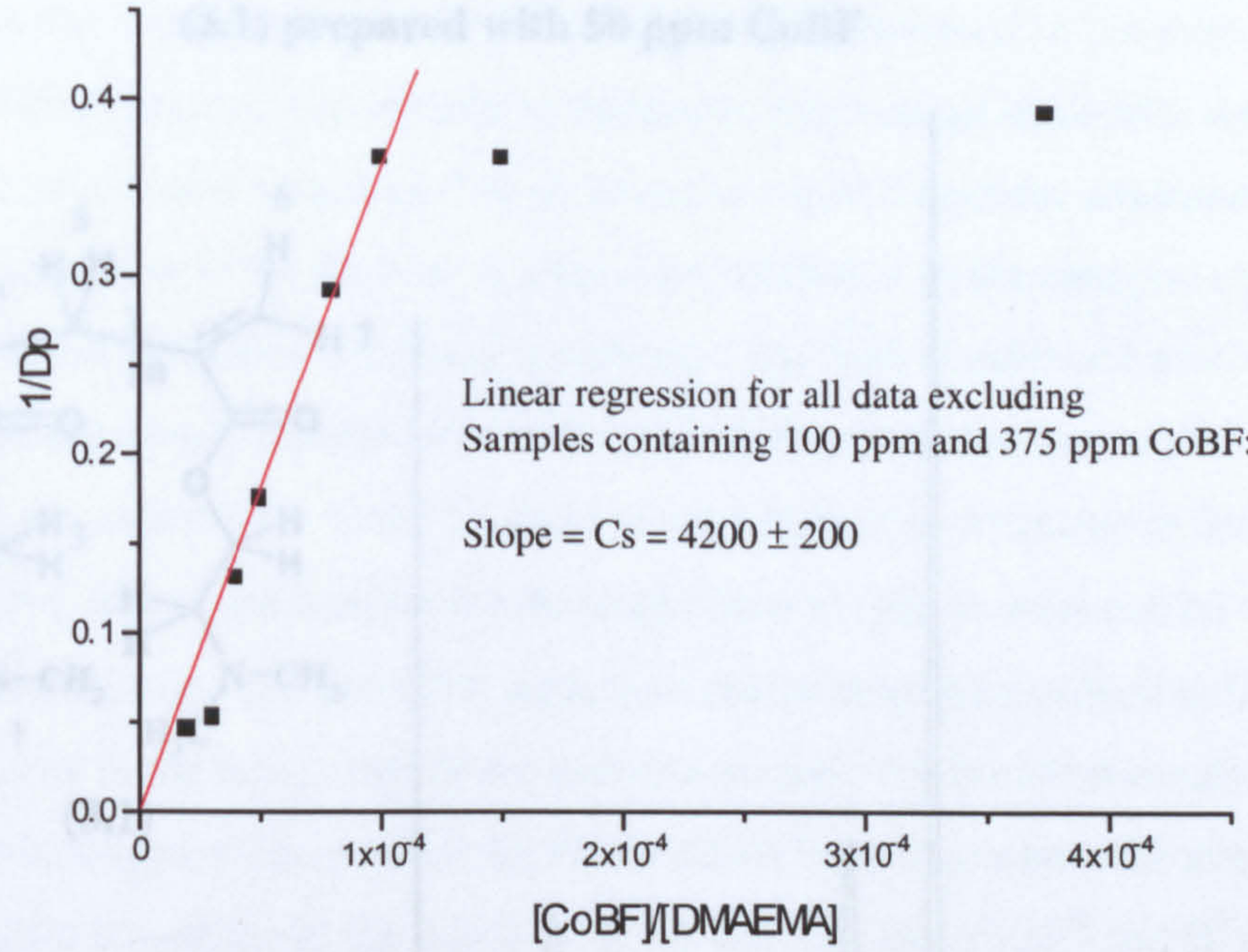
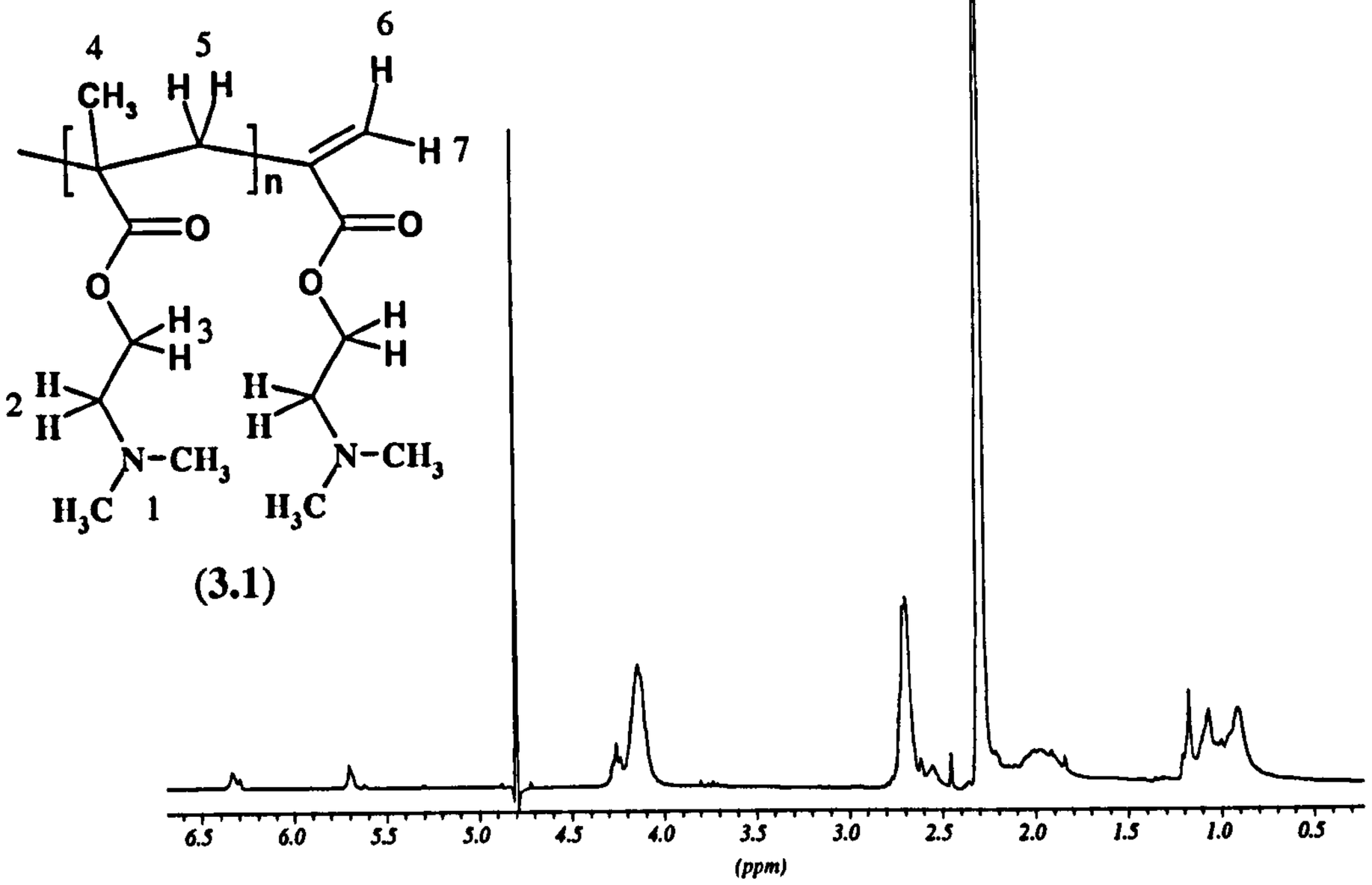


Figure 3.5 shows that for data from samples where the catalyst concentration is below 100 ppm a linear graph is obtained, i.e., where the value of the Cs is constant at 4200. At levels of catalyst above 100 ppm then no significant reduction in molecular weight is observed with increasing catalyst concentration. This may result from the catalyst solution becoming saturated resulting in a proportion of the catalyst being unable to dissolve. This reduces the concentration of catalyst available during polymerisation. Therefore the Cs is reduced, since no further reduction in the molecular weight is achieved irrespective of the catalyst concentration. The value of Cs from bulk polymerisation of DMAEMA at 70 °C agrees well with the value calculated from the Mayo plot for DMAEMA bulk polymerisation at 60 °C with low conversion that gives a Cs = 4700.

The purification of PDMAEMA macromonomer products to remove residual monomer is a complicated process. Monomer and polymer are both readily soluble in water and hexane and consequently purification by precipitation of the polymer is not possible. All products that have been prepared in this study have been purified by reduced pressure Kugelrohr distillation. Analysis of these distilled products was performed by 250 MHz ^{1}H NMR spectroscopy. The ^{1}H NMR in D_2O of the purified sample obtained from the distillation of the polymer containing 50 ppm CoBF is shown in figure 3.6

Figure 3.6 **250 MHz, ^1H NMR in D_2O of PDMAEMA macromonomer (3.1) prepared with 50 ppm CoBF**



(3.1)

Table 3.7 **Peak assignment for the 250 MHz, ^1H NMR in D_2O of PDMAEMA macromonomer (3.1) prepared with 50 ppm CoBF**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
6.33	Multiplet	1.00	H^7
5.70	Multiplet	1.54	H^6
4.80	Singlet	-	Solvent, D_2O
4.14	Broad Multiplet	16.58	H^3
2.69	Broad Singlet	16.50	H^2
2.29	Broad Singlet	54.59	H^1
1.97	Broad Multiplet	9.31	H^5
1.07	Broad Multiplet	22.45	H^4

From the ^{1}H nmr assignment it is shown that the ω-terminal vinylic functionality remains present in the sample after the removal of the monomer. The ^{1}H nmr spectrum can be used to determine the average molecular weight of the macromonomer assuming that all products contain terminal unsaturation. This assumption will hold true so long as no inhibition of the catalytic cycle occurs resulting in new termination pathways that lead to saturated products. It has been previously reported that methacrylamide undergoes a catalytic inhibition reaction with CoBF [20], this has been further investigated in Section 3.1.4. The ratio of the integral for the ω-terminal vinylic protons can be compared with another peak that represents the protons for a group contained exclusively in the repeat unit of the macromonomer. For the determination of the degree of polymerisation of the PDMAEMA macromonomer the average integral for one terminal vinyl proton of the macromonomer (H^6 and H^7) are is compared with the integral for one of the dimethylamino protons (H^1) in the repeat unit.

$$\frac{(H^1/6)}{((H^6+H^7)/2)} = \frac{(54.59/6)}{((1.00+1.54)/2)} = 7.16 = Dp$$

Multiplication of the Dp with the relative molecular mass of the repeat unit gives the average molecular weight of the macromonomer.
The Mn has been determined from the GPC and NMR analysis of a series of PDMAEMA macromonomers and the results are given in table 3.8.

Table 3.8 Comparison of NMR and GPC molecular weight analyses of PDMAEMA macromonomer (3.1) products

Sample	Mn (GPC)	Mn (NMR)
20	3400	3600
30	3100	3200
40	1200	1400
50	900	1130
80	540	550

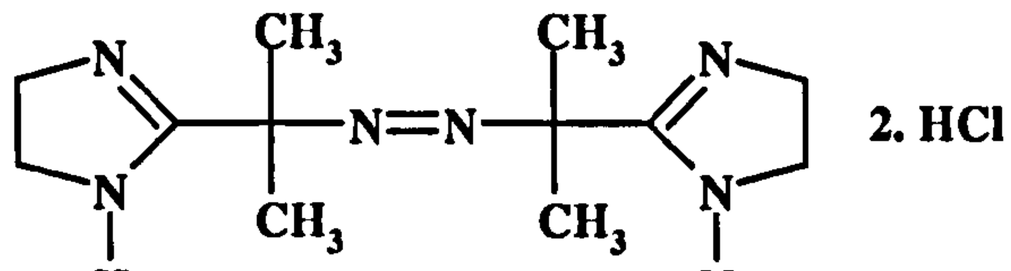
The calculated value of Mn by GPC and from ^{1}H NMR are in good agreement, however the degree of error in both methods prevents the determination of the actual degree of terminal functionality incorporated into the product.

3.1.3.2 Aqueous solution CCT mediated polymerisation of methacrylic acid

The use of water based systems in polymerisation processes has attracted much attention due to an industrial drive towards more environmentally friendly synthetic procedures. This research has investigated the CCT mediated polymerisation of hydrophilic acid based monomers in aqueous systems. Acidic monomers including methacrylic acid are incompatible with batch CCT mediated polymerisation due to acid hydrolysis of the chain-transfer agent. This research has developed new methods based on monomer and catalyst feed to establish effective and reproducible molecular weight control for the polymerisation of methacrylic acid (MAA) by fed aqueous solution CCT mediated polymerisation.

A series of experiments were performed containing different concentrations of CoBF with respect to methacrylic acid monomer. For each experiment a batch component of the reaction mixture containing free-radical initiator, water and chain-transfer agent was added to the reactor vessel. Monomer and additional transfer agent were then fed into the reaction solution over a period of 1 hour. For all of the reactions performed the amount of catalyst that was present in the batch component was always double that which was present in the feed. The reaction temperature in all cases was 55 °C and the water-soluble free-radical initiator used was 2,2'azobis(N,N'dimethyleneisobutyramidine) dihydrochloride (ADMIBA.2HCl) (**3.2**). The results are given in terms of the total chain-transfer agent present in the system.

Figure 3.7 **Water soluble free-radical initiator 2,2'azobis(N,N'dimethyleneisobutyramidine) dihydrochloride (ADMIBA.2HCl) (3.2)**



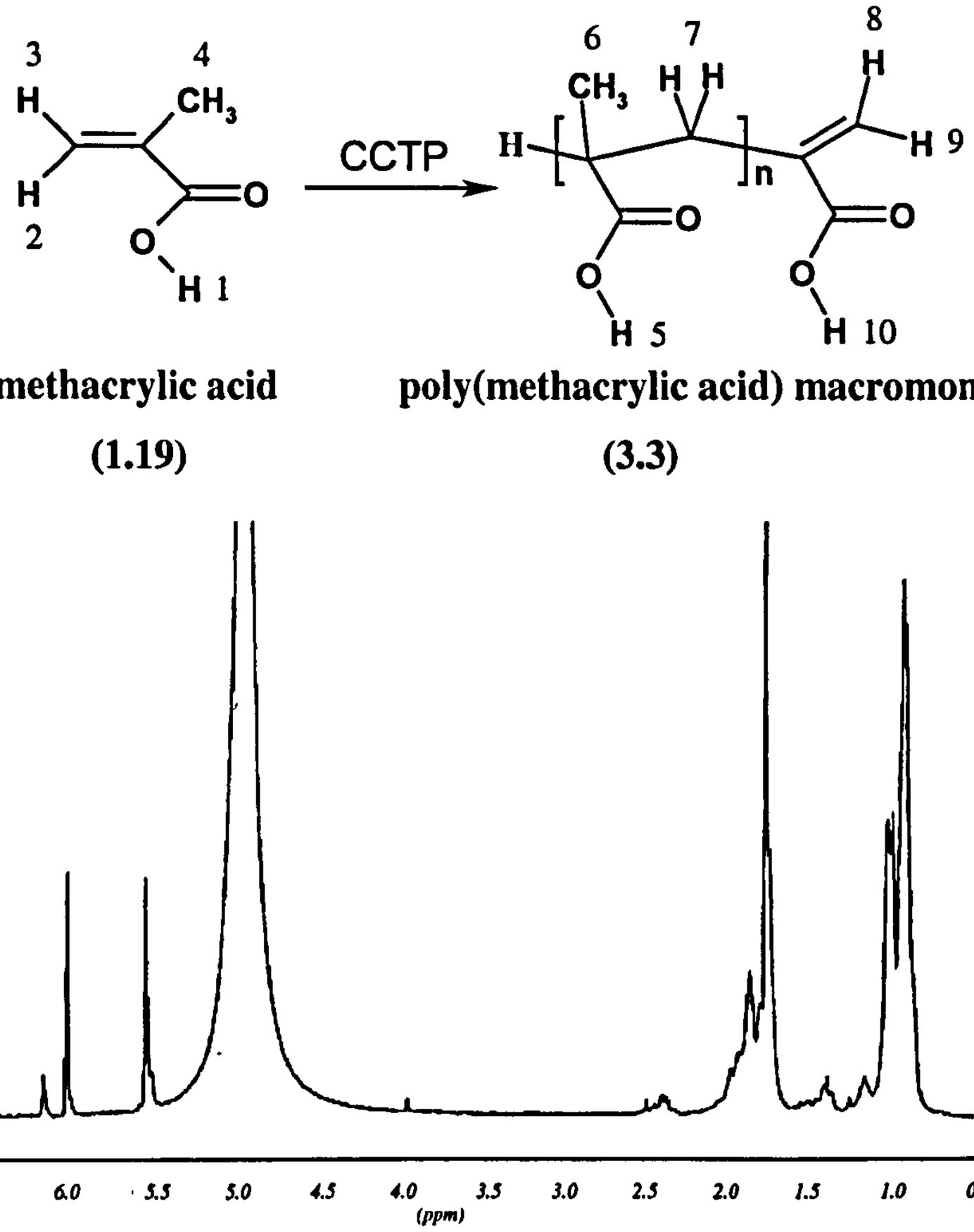
ADMIBA.2HCl (3.2)

Table 3.9 **Reaction conditions for fed aqueous solution CCT mediated polymerisation of methacrylic acid at 55 °C**

Total	Initial Reactor Charge			Feed Over 1 hour	
CoBF (ppm)	H_2O (ml)	ADMIBA.2HCl (g)	CoBF (mg)	MAA (g)	CoBF (mg)
5.9	180	0.3	1.5	74.8	0.8
27.4	180	0.3	7.0	74.8	3.6
54.7	180	0.3	14.0	74.8	7.5
120.8	180	0.3	31.2	74.8	15.6

The ^1H NMR spectrum in methanol-d^4 of the products was performed. The spectrum for the product from 27 ppm CoBF is shown in figure 3.8.

Figure 3.8 **250 MHz, ^1H NMR in Methanol-D^4 of PMAA macromonomer (3.3) prepared with 27 ppm CoBF**



methacrylic acid (1.19)

poly(methacrylic acid) macromonomer (3.3)

Table 3.10 **Peak assignment for the 250 MHz, ^1H NMR in Methanol-D^4 of the PMAA macromonomer (3.3) prepared with 27 ppm CoBF**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
6.55	Singlet	0.20	Impurity
6.14	Multiplet	1.00	H^9
6.00	Multiplet	3.79	H^2
5.60	Multiplet	4.63	H^3, H^8
4.92	Broad Singlet	-	H^1, H^5, Methanol-D^4
1.79	Broad Multiplet	41.67	H^4, H^7
0.97	Broad Multiplet	61.04	H^6

The relative integral from the ^{1}H NMR spectrum was used to determine the average molecular weight of the macromonomer and the degree of conversion obtained. The degree of conversion was calculated based on the relative integrals for the macromonomer vinyl proton H^9 compared with the vinyl proton from the monomer H^2.

$$\frac{(H^9 \text{ x Dp})}{H^2 + (H^9 \text{ x Dp})} \; x100 = \frac{(20.34)}{(3.79) + (20.34)} = 84.29\%$$

Table 3.11 gives the molecular weight and conversion data for each extract taken from the reactions performed.

Table 3.11 Molecular weight data for fed aqueous solution CCT mediated polymerisation of methacrylic acid at 55 °C

CoBF (ppm)	Extract	Mn (nmr)	% Conversion (nmr)	(gravimetry)
6	1 hour	7500	78.0	64.5
	2 hours	10400	96.4	98.7
27	1 hour	1690	60.9	59.5
	2 hours	1750	84.3	91.3
55	1 hour	850	56.9	36.4
	2 hours	1040	79.4	85.4
121	1 hour	500	51.2	46.2
	2 hours	610	58.2	56.7

Figure 3.9 Pseudo Mayo plot for fed aqueous solution CCT mediated polymerisation of methacrylic acid at 55 °C

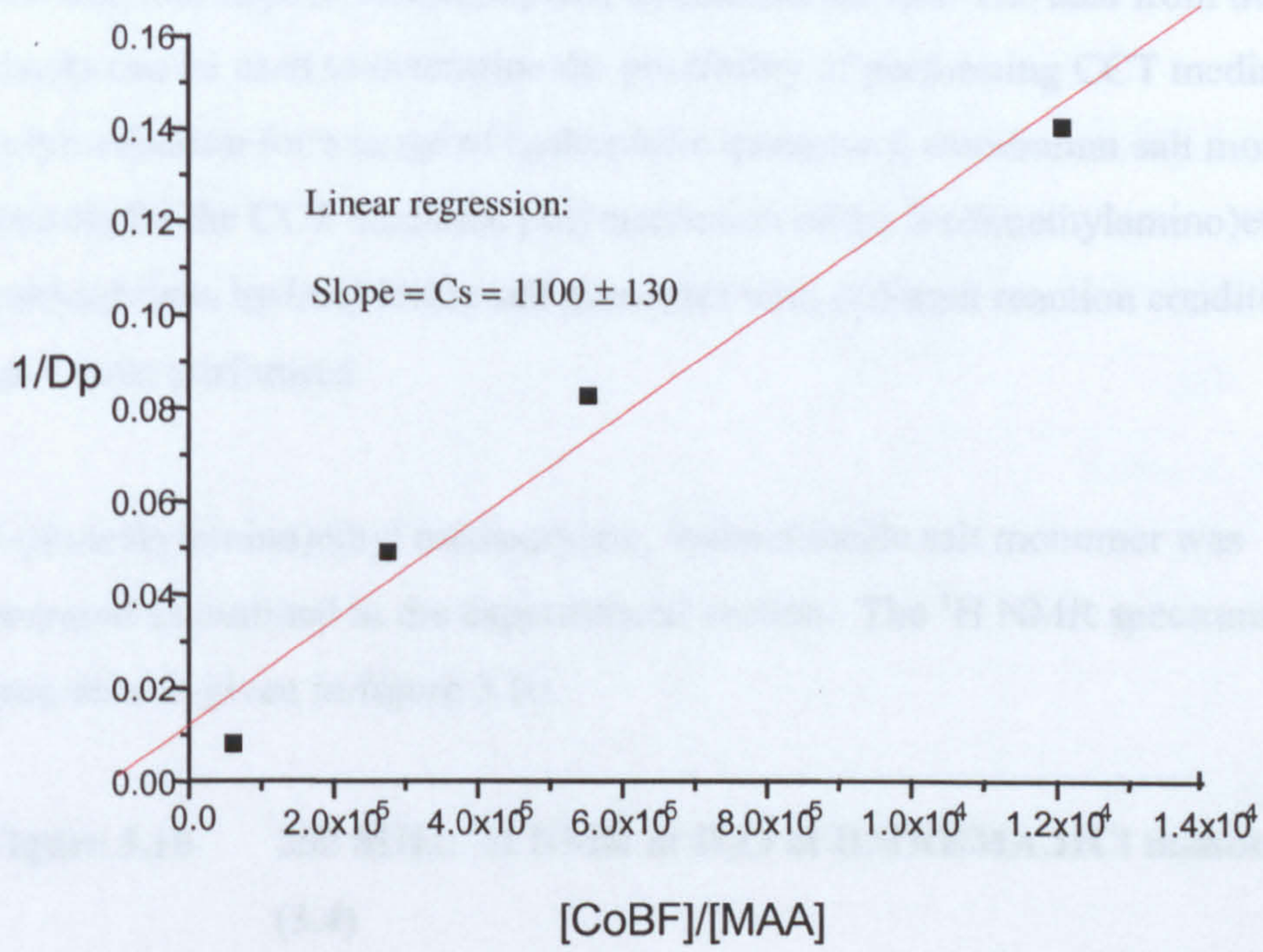


Figure 3.9 shows that a linear graph is obtained for a pseudo Mayo plot for fed aqueous solution CCT mediated polymerisation of methacrylic acid at 55 °C. A linear graph represents a situation where the value of Cs is constant for the range of catalyst concentrations investigated. As the relative concentration of transfer agent is increased with respect to monomer, the rate of polymerisation is reduced. The instantaneous conversion data for each reaction shows that, as the amount of catalyst is increased, the rate of reaction is reduced.

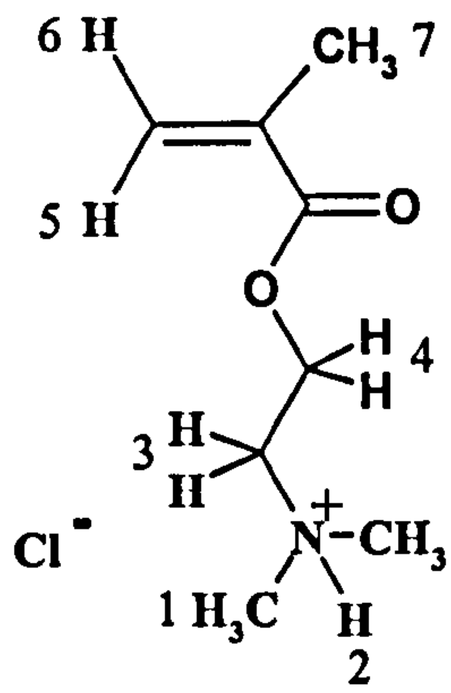
3.1.3.3 Aqueous solution CCT mediated polymerisation of the hydrochloric acid salt of DMAEMA monomer

This section outlines the results from a study to determine the possibility of performing aqueous CCT mediated polymerisation of DMAEMA monomer using fed reaction procedures based on those performed with methacrylic acid. DMAEMA monomer is hydrolytically unstable in water, undergoing self-induced base catalysed monomer decomposition [21]. This research has

investigated the possibility of performing aqueous CCT mediated polymerisation of the "protected" DMAEMA monomer, 2-(dimethylamino)ethyl methacrylate, hydrochloride salt. The data from these` results can be used to determine the possibility of performing CCT mediated polymerisation for a range of hydrophilic quaternary ammonium salt monomers. Results for the CCT mediated polymerisation of the 2-(dimethylamino)ethyl methacrylate, hydrochloride salt monomer with different reaction conditions have been performed.

2-(dimethylamino)ethyl methacrylate, hydrochloride salt monomer was prepared as outlined in the experimental section. The ^{1}H NMR spectrum of the monomer is given in figure 3.10.

Figure 3.10 250 MHz, ^{1}H NMR in D_2O of DMAEMA.HCl monomer (3.4)



(3.4)

Table 3.12 Peak assignment for the 250 MHz, ^1H NMR spectrum in D_2O of the DMAEMA.HCl monomer

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
6.78	Singlet	1.00	H^5
5.65	Singlet	1.00	H^6
4.60	Singlet	-	Solvent, D_2O
4.43	Triplet	2.01	H^4
3.45	Triplet	2.04	H^3
2.87	Singlet	6.17	H^1
2.13	Singlet	0.15	Acetone Impurity
1.82	Singlet	2.95	H^7

The proton attached to the quaternary nitrogen (H^2) undergoes slow exchange and is observed as a broad peak downfield at $\delta > 7.0$. A series of initial CCT mediated polymerisations based on previous reactions with methacrylic acid were performed. An aqueous solution of monomer and chain transfer agent was prepared and this was then fed into a reaction vessel containing chain transfer agent, water and initiator over a period of 1 hour. The initiator that was used for these experiments was ADMIBA.2HCl (**3.2**). All reactions were performed at pH 7 and at 55 °C. Four reactions were performed with varying concentrations of the chain transfer agent (CoBF) with respect to monomer. A reaction containing no CoBF was performed as a control experiment.

Table 3.13 Reaction conditions for fed aqueous solution CCT mediated polymerisation of DMAEMA.HCl at pH 7 and 55°C

Total	Initial Reactor charge			Feed Over 1 hour		
CoBF (ppm)	H_2O (ml)	ADMIBA.2HCl (mg)	CoBF (mg)	DMAEMA.HCl (g)	CoBF (mg)	H_2O (ml)
0	10	0.011	0	5.81	0	35
29	10	0.011	0.28	5.81	0.11	35
58	10	0.011	0.55	5.81	0.23	35
122	10	0.011	1.10	5.81	0.54	35

Table 3.14 Conversion data for fed aqueous solution CCT mediated polymerisation of DMAEMA.HCl (3.4) at pH 7 and 55°C

CoBF (ppm)	Extract	% Conversion (NMR)
0	1 hour	98.5
	2 hours	98.7
29, 58, 122	2 hours	For all reactions no polymer was obtained after 2 hours

The control reaction that contained no chain transfer agent showed that almost complete consumption of the monomer had occurred within 1 h. All reactions that contained chain transfer agent showed no formation of polymer.

Acidic monomers such as methacylic acid are known to poison the chain transfer agent, CoBF through hydrolysis reactions. The successful CCT mediated polymerisation of methacrylic acid monomer is established by maintaining the relative concentration of the chain transfer agent under fed conditions. The analogous fed reaction at pH 7 for the DMAEMA.HCl

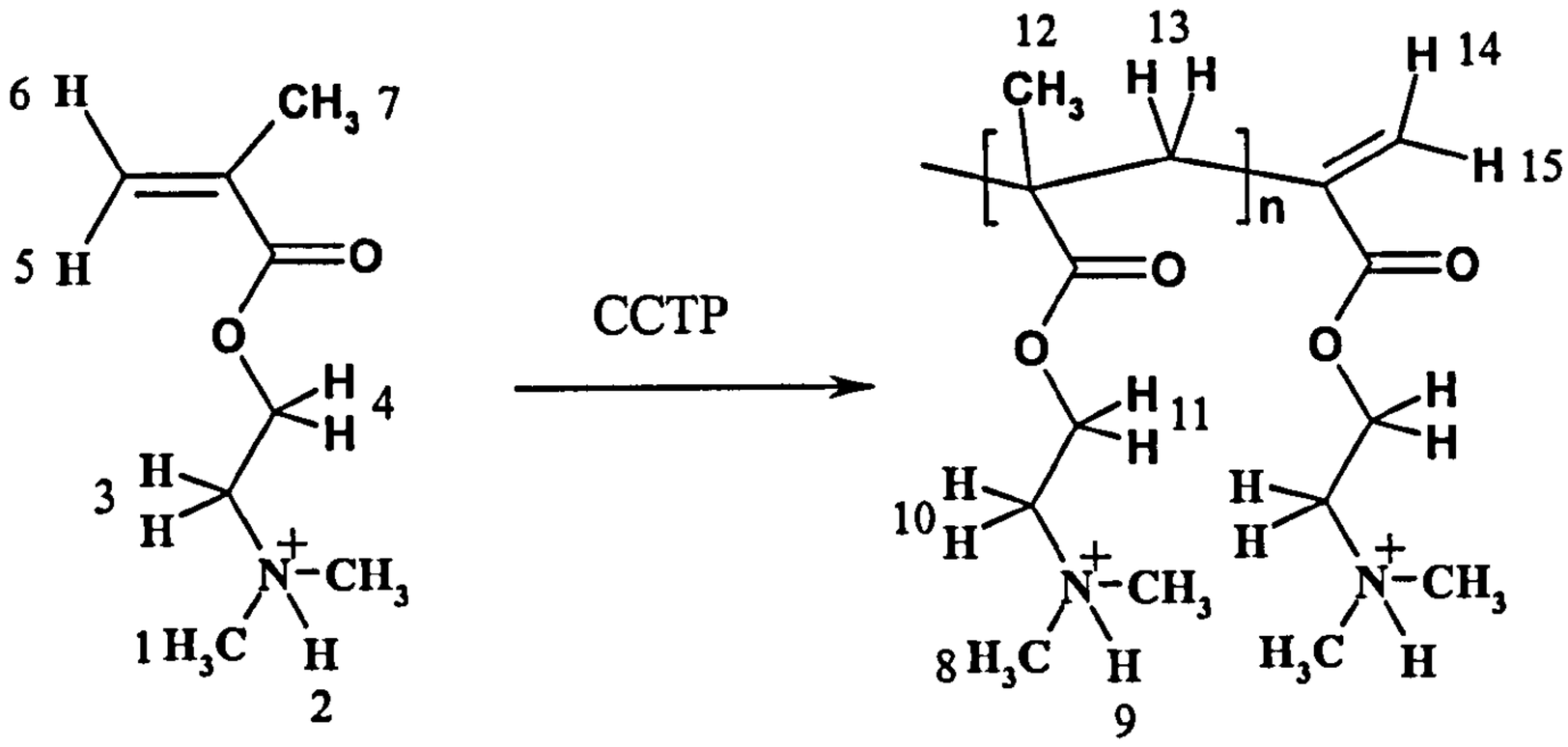
quaternary monomer was shown to yield no polymer in the presence of the chain-transfer agent.

A series of experiments were performed to established if CCT mediated polymerisation of the DMAEMA.HCl monomer could be performed by variation of the feed solution pH. Two new aqueous monomer stock solutions were prepared with the addition of 0.1 M aqueous hydrochloric acid to an aqueous monomer stock, where the solution pH was monitored with the use of a digital pH meter equipped with a glass combination electrode. The resulting stock solutions had final pH's of 5 and 3.5 respectively. Fed CCT mediated polymerisation of these monomer stock solutions was performed with CoBF at 29 ppm using identical reaction conditions to those that were used for the polymerisation of the DMAEMA.HCl monomer at pH 7.

Table 3.15 Reaction conditions for fed aqueous solution CCT mediated polymerisation of DMAEMA.HCl (3.4) at pH 3.5 and pH 5 at 55 °C

	Total	**Initial Reactor Charge**			**Feed** Over 1 hour		
pH	CoBF (ppm)	H_2O (ml)	ADMIBA.2HCl (mg)	CoBF (mg)	DMAEMA.HCl (g)	CoBF (mg)	H_2O (ml)
5	29	10	0.011	0.28	5.81	0.11	35
3.5	29	10	0.011	0.28	5.81	0.11	35

Figure 3.12 **250 MHz, ^{1}H NMR in Methanol-D^4 of the product from the polymerisation of DMAEMA.HCl macromonomer (3.5) prepared with 29 ppm COBF at pH 5 after 4 hours**



(3.4) (3.5)

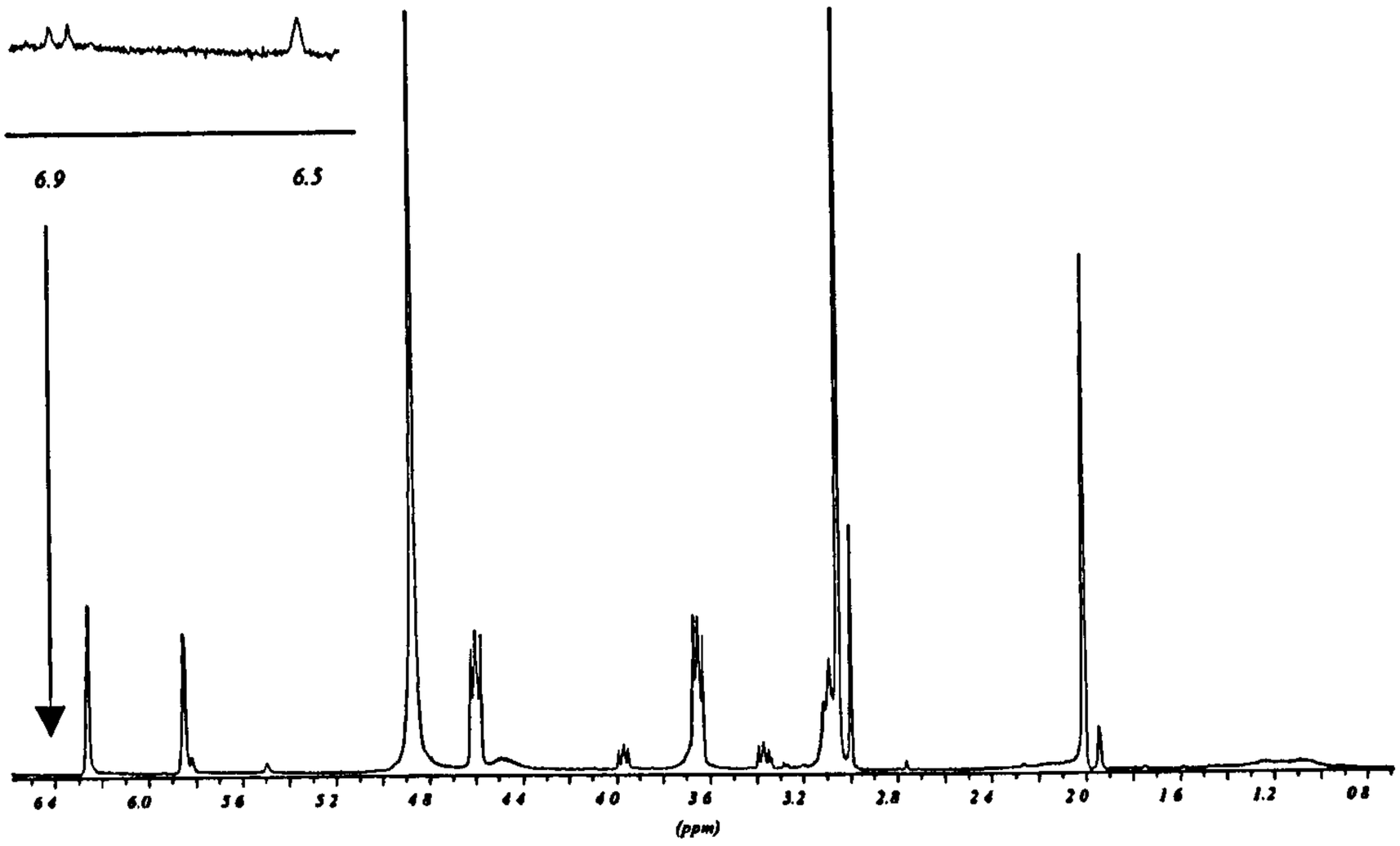


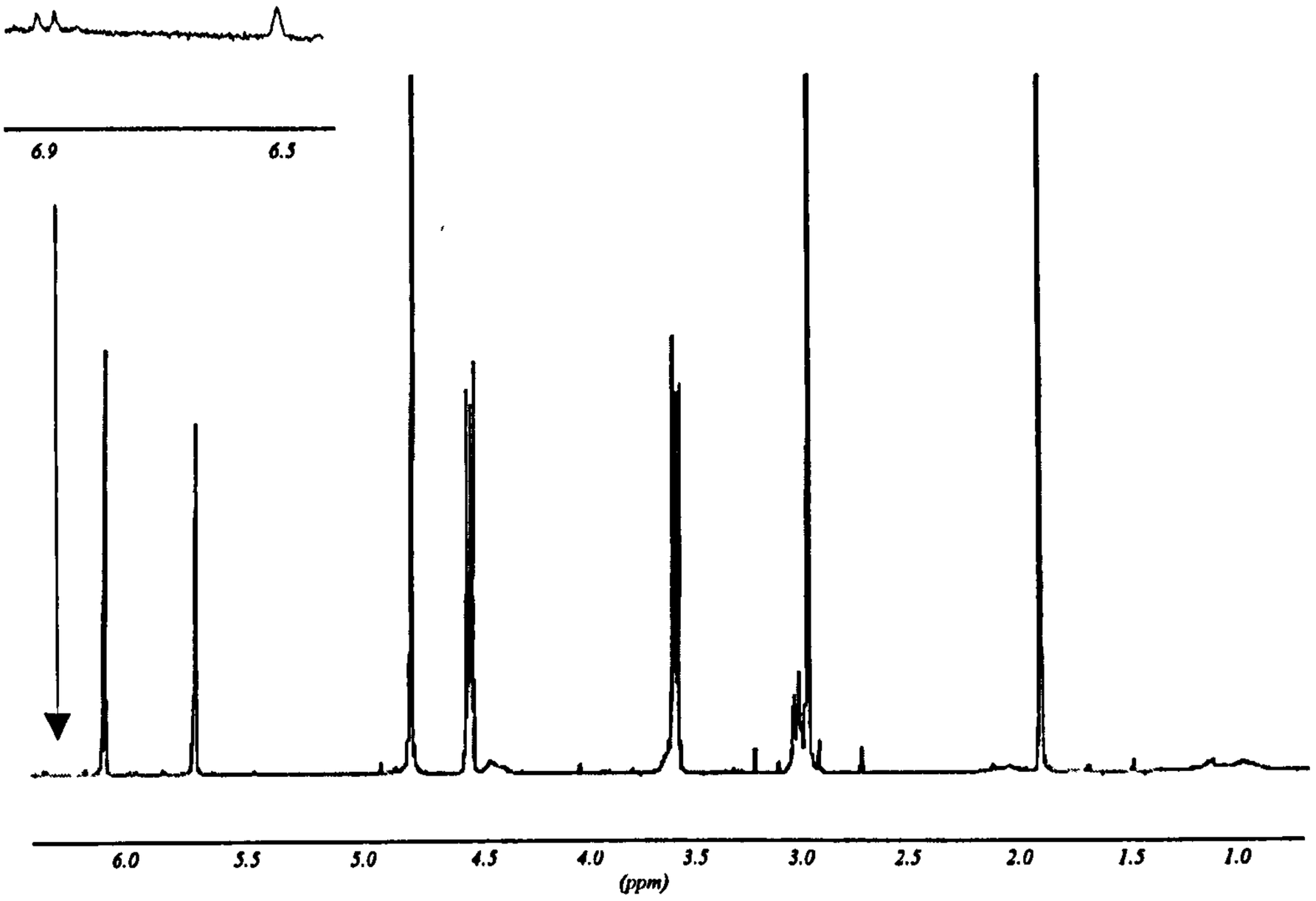
Table 3.16 Peak assignment for the 250 MHz, ^1H nmr spectrum in D_2O of the DMAEMA.HCl macromonomer species formed from polymerisation at pH 5

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
6.89	Doublet	0.10	H^{14}
6.50	Singlet	0.11	H^{15}
6.19	Singlet	22.19	H^{5}
5.77	Singlet	19.34	H^{6}
5.75	Singlet	1.85	(impurity)
5.43	Singet	1.15	(impurity)
4.80	Broad Singlet	-	Solvent, D_2O
4.53	Broad Triplet	42.54	H^{4}
4.39	Broad Singlet	6.65	H^{11}
3.88	Triplet	6.20	(impurity)
3.56	Broad Triplet	53.84	H^{3}, H^{10}
3.30	Triplet	19.09	(impurity)
3.02	Broad Multiplet	169.17	H^{1}, H^{8}
2.93	Singlet	19.09	(impurity)
1.94	Singlet	67.62	H^{13}, H^{7}
1.87	Singlet	5.67	(impurity)
1.12	Multiplet	17.59	H^{12}

The protons attached to quaternary nitrogen atoms, H^2 and H^9 undergo slow exchange and are observed as a broad peaks downfield at $\delta > 7.0$.

The ^1H NMR spectrum of the products from the reaction at pH 5 after 4 hours gives peaks that are assigned as unreacted monomer (DMAEMA.HCl) (**3.4**), macromonomer (**3.5**) and a series of new peaks (impurity) equivalent to those found in the monomer but with a relative shift upfield. The splitting pattern and shift of these new peaks suggests that monomer decomposition has occurred.

Figure 3.13 **250 MHz, ^{1}H NMR in Methanol-D4 of the product from the polymerisation of DMAEMA.HCl macromonomer (3.5) prepared with 29 ppm CoBF at pH 3.5 after 4 hours**



The ^{1}H NMR spectrum of the products from the reaction at pH 3.5 after 4 hours shows only the formation of peaks representing monomer (**3.4**) and macromonomer (**3.5**). No peaks representing monomer decomposition products are detected.

The degree of polymerisation and the degree of conversion were determined for all samples based on the NMR analysis. Determination of the relative integral of H^{11} in comparison to H^{15} and H^{14} allows calculation of the degree of polymerisation. The determination of the relative integral for the macromonomer vinylic protons (H^{15} and H^{14}) in comparison with the vinylic protons from the monomer (H^{6} and H^{5}) allows for a determination of conversion, in this case two conversions are calculated for the samples from the reaction at pH 5. A calculation based on the relative integral for monomer not including those peaks representing monomer decomposition was performed and

a second calculation took into account the integral for the decomposition products.

Table 3.17 Molecular weight data for fed aqueous solution CCT mediated polymerisation of DMAEMA.HCl (3.4) with 30 ppm CoBF at 55°C with controlled pH

pH	Extract	Mn (NMR)	% Conversion calculation based on no decomposition (NMR)	% Conversion calculation with decomposition products included (NMR)
5	2 hours	-	5.4	2.4
	4 hours	6100	13.8	7.5
	24 hours	9930	34.2	33.0
3.5	2 hours	1240	3.9	-
	4 hours	2500	10.5	-
	24 hours	4750	28.4	-

The molecular weight data show that, as the pH is reduced, more effective molecular weight reduction is obtained. This trend suggests that catalytic efficiency is increased at lower pH. These results are contrary to the data observed with methacrylic acid monomer, where at low pH poisoning of the catalyst occurs, resulting in an increase in average degree of polymerisation. The data show that, when the monomer feed pH is changed, no appreciable change in the instantaneous conversion occurs.

From the NMR analyses of the polymerisation products it is shown that at pH 3.5 the DMAEMA.HCl monomer (**3.4**) is stable under reaction conditions. As the pH is increased some undesired decomposition of monomer occurs. This process is accompanied by an inhibition of the catalyst activity and results in an increase in the molecular weight of the macromonomer. The reaction at pH 7 produced only monomer and monomer decomposition products. The rates of polymerisation for all reactions are significantly lower in comparison to analogous reactions performed with methacrylic acid.

A series of new experiments were performed to determine whether alteration of the experimental parameters would provide more efficient control over the polymerisation method. Variation of the monomer feed time and reaction temperatures were examined, the results from these tests are summarised in table 3.18.

Variations of the reaction containing 29 ppm CoBF at pH 5 were performed. All reagents are included at the same weight % as outlined in table 3.15.

Table 3.18 Effect on the molecular weight and conversion of changes in reaction temperature and feed time for the CCT mediated polymerisation of DMAEMA.HCl monomer (3.4)

Variable		Extract (4 hours)	
Temperature (°C)	Feed Time (hours)	Mn (NMR)	Conversion (%)
55	1	6100	13.8
55	3	1700	9.2
70	1	3900	20.0

These results show that through variation of the reaction conditions that a significant alteration to the degree of molecular weight reduction can be obtained. However no method was found to provide an effective increase in the degree of conversion. The NMR spectra of all reactions showed the formation of monomer decomposition products.

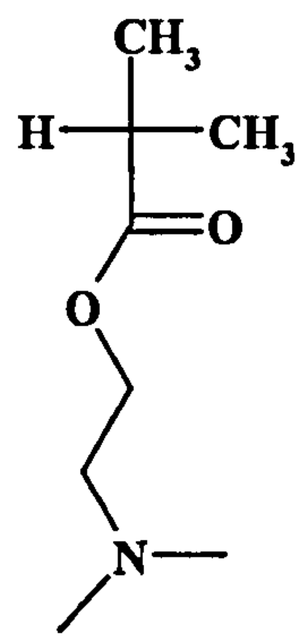
From the results obtained for the CCT mediated polymerisation of DMAEMA.HCl macromonomer (**3.5**) it has been shown that it is possible to produce macromonomer products in low yield. Purification of the quaternary salt monomer is complicated due to the similarity between the properties of the monomer and the macromonomer. Washing the products in base to produce the free PDMAEMA monomer and macromonomer allows purification by

distillation. This is however a complicated procedure and therefore the synthesis of PDMAEMA macromonomers for further co-polymerisation has concentrated on bulk polymerisation methods, outlined in section 3.1.3.1.

3.1.4 Investigation of the interaction between with 2-(dimethylamino)ethyl isobutyrate (DMAEIB) (3.6) and CoBF (1.11)

Section 3.1.2.2 showed that at a certain concentration where the [CoBF]/[DMAEMA] ratio is ~75 x 10^{-7} then the stock solution whilst undergoing freeze/pump/thaw degassing changed colour from a clear orange solution to a dark blue solution. This change in colour is indicative of a change in the oxidation state for the Co metal centre. The visible spectra of CoBF with the saturated hydrogenation product of DMAEMA monomer; 2-(dimethylamino)ethyl isobutyrate (DMAEIB) (**3.6**) was investigated to determine the effect of the tertiary amine functionality on the chain transfer agent (CoBF) without the occurrence of polymerisation. DMAIEB was prepared from the DMAEMA monomer as outlined in the experimental section.

Figure 3.13 2-(dimethylamino)ethyl isobutyrate (DMAEIB) (3.6)



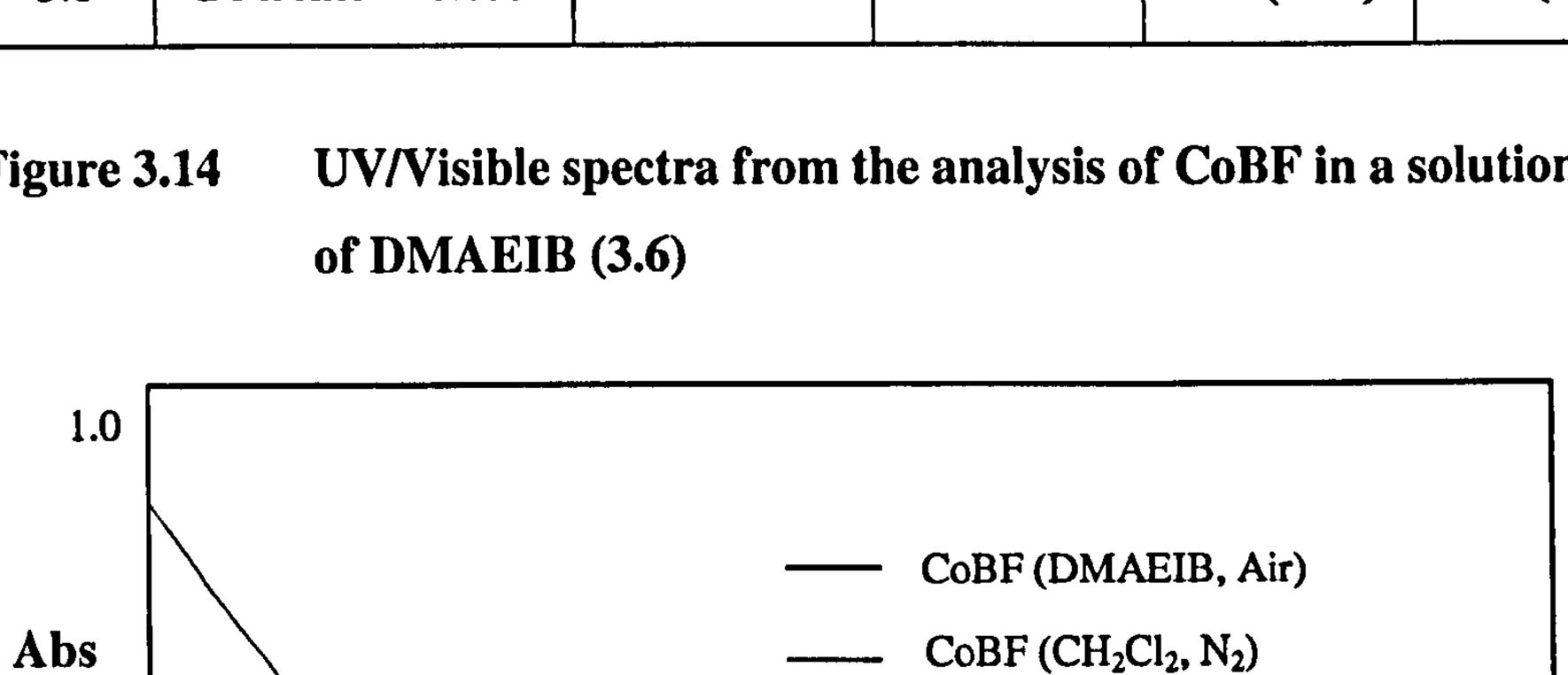
DMAEIB (**3.6**)

Three different solutions were examined by UV/Visible spectroscopy. Stock solutions of CoBF in dichloromethane and CoBF in DMAEIB were prepared under deoxygenated conditions. The visible spectra of these solutions were recorded. The stock solution containing DMAEIB was opened to the atmosphere and left to stand for 6 hours. The visible spectrum of the resulting solution was determined. The composition and analyses of these solutions is outlined in table 3.19.

Table 3.19 Composition of standards for UV/Visible spectroscopic analysis

Composition			λ-max (Abs)		
			nm (Abs)	nm (Abs)	nm (Abs)
CoBF (mg)	**Solvent** Type (ml)	**Atmosphere**	**Band 1**	**Band 2**	**Band 3**
5.0	CH_2Cl_2 0.125	N_2	448 (0.57)	590 (0.12)	754 (0.02)
5.0	DMAEIB 0.125	N_2	450 (0.10)	582 (0.39)	694 (0.37)
5.0	DMAEIB 0.125	Air	-	580 (0.27)	676 (0.18)

Figure 3.14 UV/Visible spectra from the analysis of CoBF in a solution of DMAEIB (3.6)



The visible absorption spectrum of CoBF in dichloromethane with an inert nitrogen atmosphere shows one major absorption band at 448 nm. Gridnev *et al* assign the absorption band of a related low spin Co(II) macrocycle as 460 nm [15]. The band observed at 448 nm for CoBF in dichloromethane is assigned as Co(II). The analogous visible spectrum obtained for CoBF in DMAEIB shows a small Co(II) band at 450 nm and two new more intense bands at 582 nm and 694 nm. According to Schrauzer and Holland the Co(I) band lies in the range from 600-700 nm [22]. Gridnev *et al* assign a Co(I) band at 750 nm and a prominent isobestic point at 580 nm [15]. The bands observed for CoBF with DMAEIB at 582 nm and 694 nm are assigned as Co(I) species. Co(III) is found at 410 nm in the visible spectrum, this is only detected for the sample containing CoBF with DMAIEB with an air atmosphere. Thus this study shows that a change in the oxidation state of the Co catalyst occurs when a solvent containing a tertiary amine is added. The reduced catalytic activity of CoBF with DMAEMA in comparison to MMA may be the result of redox reaction between the Co catalyst and the monomer producing a new catalyst-monomer complex. The formed species is stable in an inert nitrogen atmosphere but is shown to decompose to form Co(I) in air.

3.2 CONCLUSION

The chain transfer constant of DMAEMA with CoBF has been evaluated with high reproducibility. A series of PDMAEMA macromonomers have been prepared from bulk CCT mediated polymerisation. Reproducible control over the molecular weight of the macromonomer product was attained. The conversions for all bulk CCT mediated polymerisations of DMAEMA were low. CCT mediated polymerisation of DMAEMA.HCl monomer was shown to be pH dependent where at pH 5 or higher then significant monomer decomposition occurred. A series of PMAA macromonomers have been successfully prepared with reproducible results for predicting the molecular weight of the macromonomer formed. High conversion was attained for all reactions.

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Chapter 4

SYNTHESIS OF CO-POLYMERS FROM CCT MACROMONOMERS

There is no such thing as a failed experiment,

only experiments with unexpected outcomes.

Buckminster Fuller

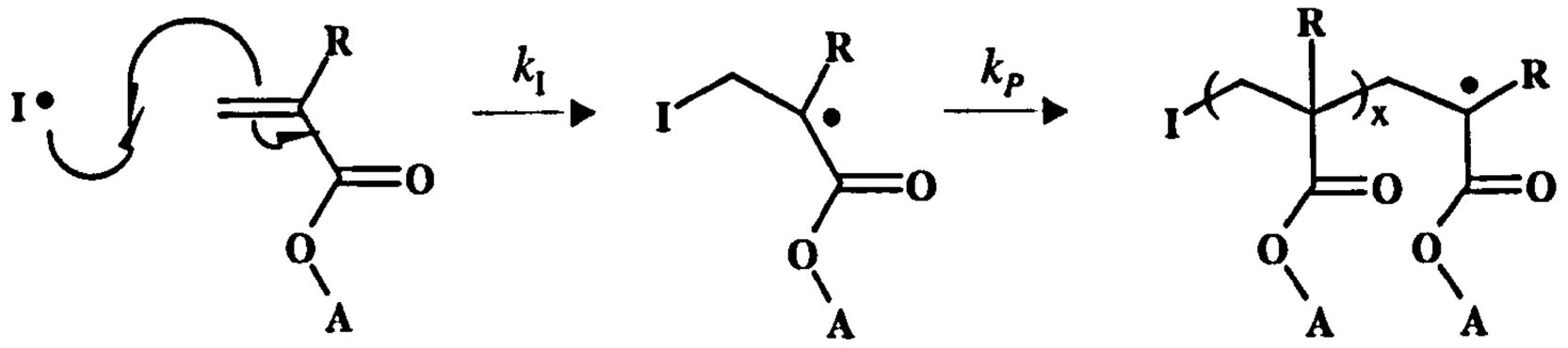
4.0 INTRODUCTION

The free-radical polymerisation of a macromonomer that contains ω-terminal unsaturation with an acrylic monomer can be used to establish conformational control in the co-polymer product. A simplified mechanism based on those originally proposed by Rizzardo *et al* for the co-polymerisation of an acrylic monomer with a CCT macromonomer is considered [1,2].

Free-radical initiation of an acrylic co-monomer containing functionality [A] produces a new growing homopolymer of [A] (figure 4.0).

Figure 4.0 Initiation and propagation of co-monomer [A]

Initiation of co-monomer

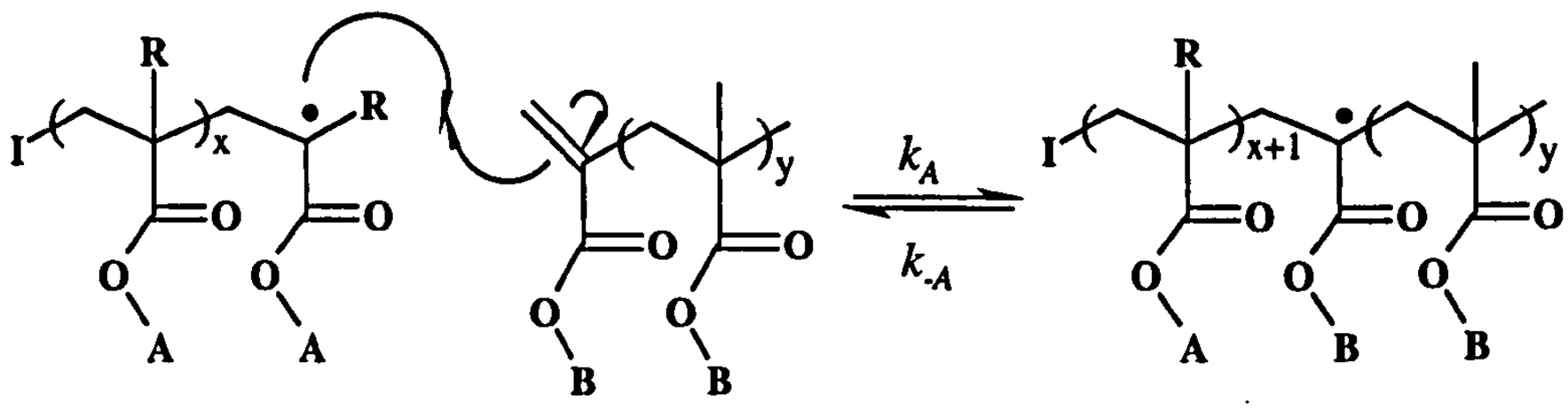


growing homopolymer chain

k_I and k_P are the respective rate constants for initiation and propagation of an acrylic monomer containing functionality [A].

The addition reaction of a CCT macromonomer containing functionality [B] with the propagating homopolymer of [A] produces a hindered tertiary carbon-centred radical (figure 4.1).

Figure 4.1 Reaction of CCT macromonomer [B] with a growing homopolymer [A]



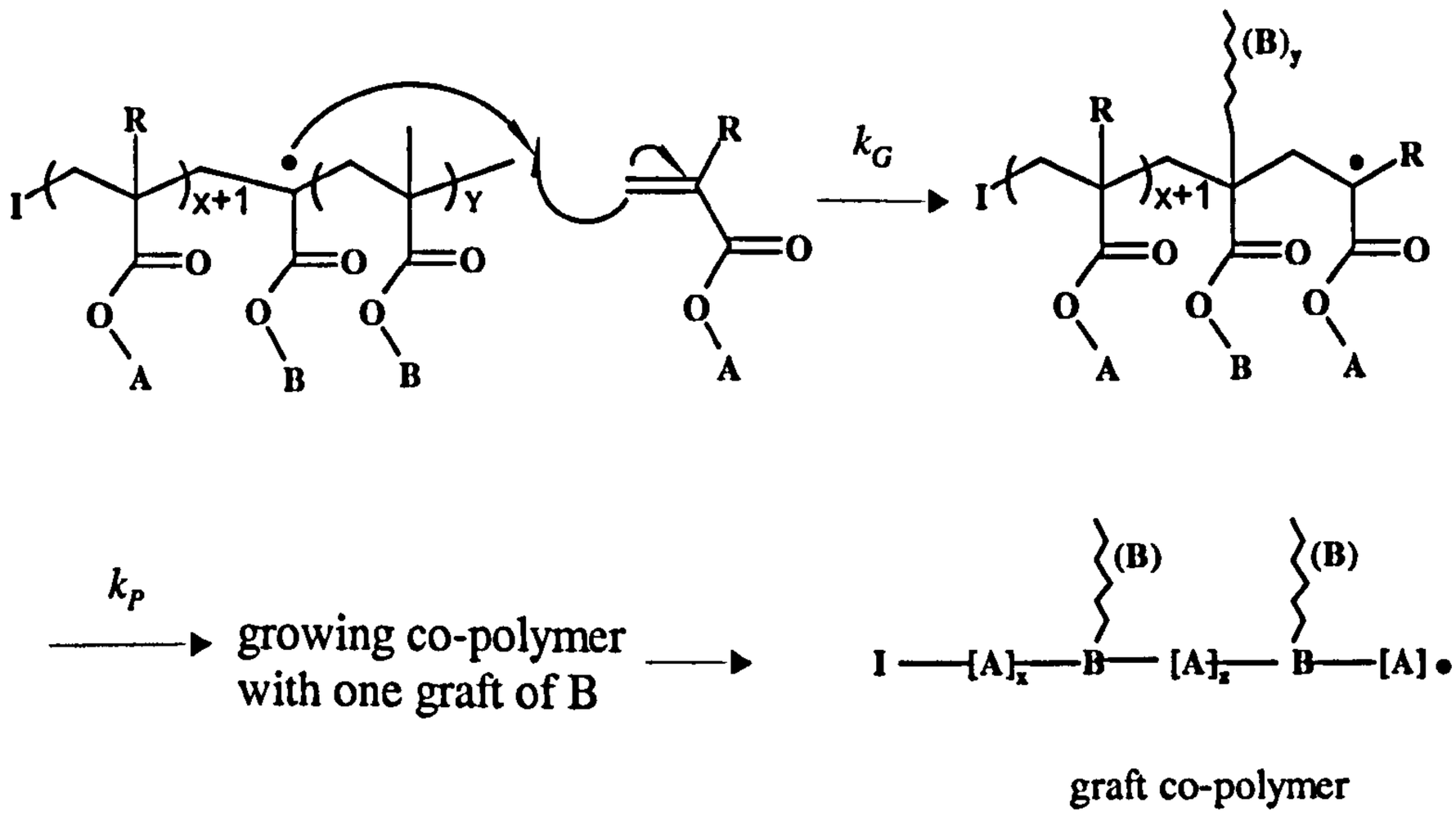
k_A is the rate constant for the addition reaction of a growing homopolymer of [A] with a CCT macromonomer containing [B].

The hindered tertiary carbon centred radical can undergo three different reactions:

1) β-scission along the polymer backbone can result in a reversible depropagation step to produce the starting materials (figure 4.1), with a rate constant k_{-A}.

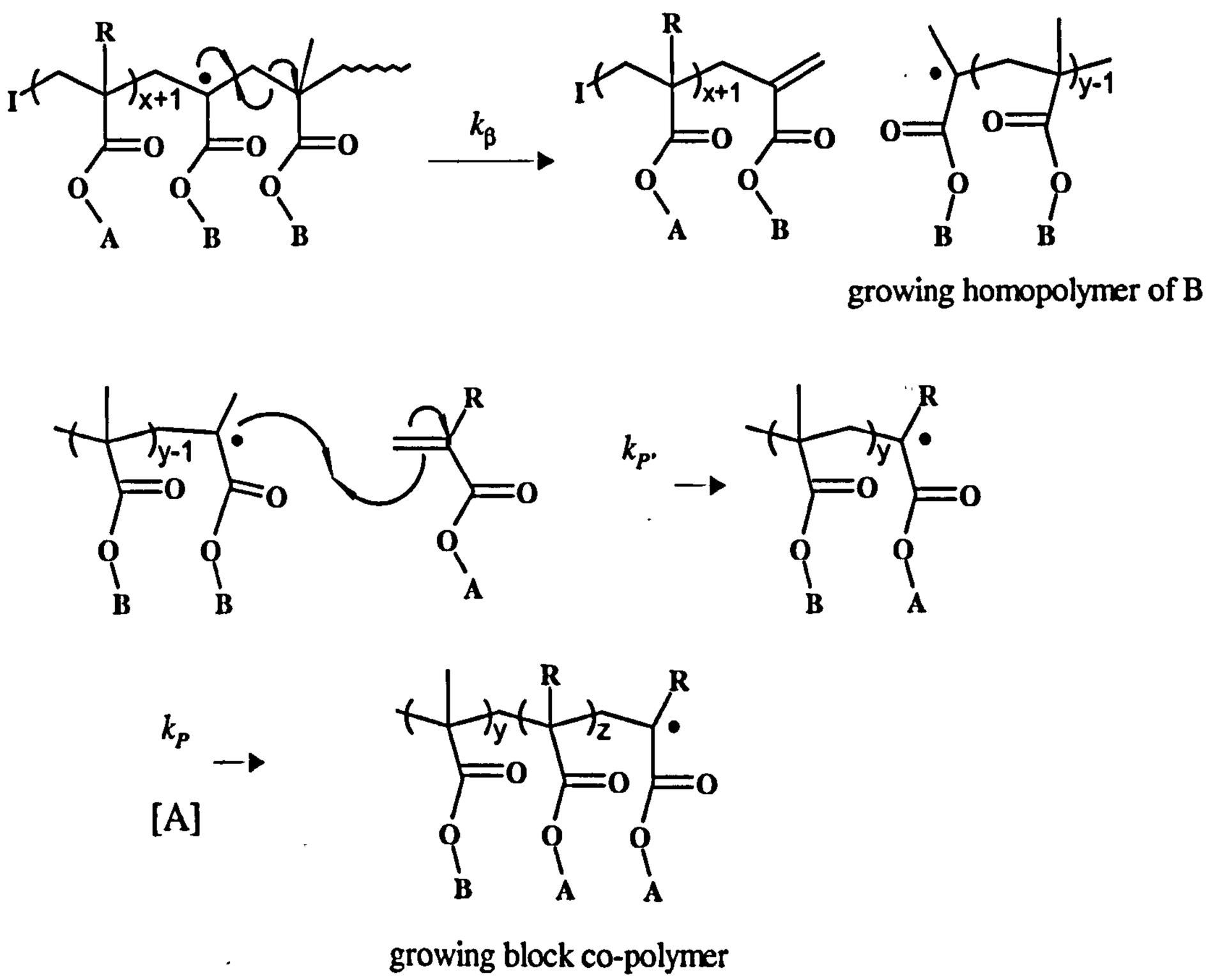
2) The tertiary carbon-centred radical can co-polymerise with a monomer containing [A] to form a graft of [B] to the growing homopolymer of [A] (figure 4.2) [3,4]. The rate constant for graft formation is k_G.

Figure 4.2 Graft co-polymer synthesis (pathway 2)



2) When the tertiary carbon centred radical is sufficiently bulky then the rate of propagation reaction with co-monomer to form grafts (K_G) is reduced. Fragmentation of the chain by a β-scission mechanism (figure 4.3) produces a terminally unsaturated macromonomer comprising polymer [A] with an ω-unsaturated end group of [B] together with a growing homopolymer of [B] [5]. The rate constant for this β-scission mechanism is k_β. The growing homopolymer of [B] can propagate polymerisation with monomer [A] to produce an [AB] block co-polymer [6]. The fragmentation pathway k_β can be considered as a type of chain-transfer reaction, where a new propagating radical is formed and the original propagating species is terminated. As with conventional chain-transfer the addition of macromonomer as a chain-transfer agent to a radical polymerisation is accompanied with a reduction in the average degree of polymerisation.

Figure 4.3 Block co-polymer synthesis (pathway 3)



Where no selectivity in the reaction pathway is observed then k_G and k_β are in competition and co-polymerisation results in a mixture of graft and block co-polymer species. Rizzardo *et al* showed that for the co-polymerisation of methyl methacrylate macromonomer with methyl methacrylate monomer that propagation of the tertiary carbon centred radical addition product with methyl methacrylate does not occur under standard reaction conditions [1]. Where R is an alkyl group then the hindered tertiary carbon centred radical is sufficiently stable such that the rate of propagation is reduced. Fragmentation of the chain is shown to occur by β-scission (k_β), resulting in the formation of a propagating radical species and a new vinylic macromonomer. This chain-transfer step has been shown to reduce the molecular weight of the product polymer in comparison with products obtained in the absence of macromonomer [7-9]. Co-polymerisation of the new propagating radical species with monomer ($k_{P\cdot}$) results in the formation of block co-polymer species [10]. Meijs and Rizzardo proposed that, when the co-monomer is an acrylate (i.e., where R is a proton), then the reduction in steric bulk at the radical centre will significantly increase the rate of propagation with co-monomer (K_G) and therefore favour the formation of graft co-polymer products [4]. Caicoli *et al* have reported that for reactions of methyl methacrylate macromonomer with a selection of common co-monomers including styrene, ethyl acrylate and acrylonitrile that all products have a significant reduction in molecular weight in comparison to their homopolymers prepared in the absence of macromonomer [1]. This reduction in the molecular weight was attributed to the large degree of steric bulk at carbon centred radical (figure 4.1) reducing the rate of polymerisation with the co-monomer. The tertiary carbon centred radical undergoes β-scission of the polymer backbone that leads to chain transfer and the observed reduction in molecular weight.

The degree of chain transfer that occurs for co-polymerisation of methacrylate monomers with macromonomers can be determined by measuring the chain-transfer co-efficient, Cs (section 1.5.1.1). The chain-transfer co-efficient is a measure of the relative rate of the transfer reaction (k_{tr}) in comparison with the rate of propagation (k_P).

$$Cs = \frac{k_{tr}}{k_p} \qquad (4.0)$$

Section 1.5.1.1 showed how the Mayo equation (1.7) could be used to determine the Cs for chain transfer agents.

$$\frac{1}{Dp} = \frac{1}{Dp_0} + Cs\frac{[T]}{[M]} \qquad (1.7)$$

The Mayo equation can only be used to accurately determine the Cs for reactions where the chain-transfer step does not affect the rate of polymerisation. Addition of a macromonomer to a propagating polymer produces a hindered tertiary carbon centred radical (figure 4.1). Reversible depropagation of the tertiary carbon centred radical can occur by a β-scission mechanism (figure 4.1). This reversible equilibrium alters the rate of polymerisation and consequently the value of Cs obtained from the Mayo equation is subject to a degree of error. A Mayo plot for the determination of the chain-transfer co-efficient of a macromonomer results in a curve rather than a linear plot. Suddaby *et al* derived a new expression for the determination of Cs in the presence of a macromonomer, taking into account changes in conversion due to the concentration of macromonomer (equation 4.1) [11].

$$Dp = \frac{[M]_0 P}{(2 - F_C) f [I]_0 (1 - \exp(-k_{dt})) + Cs[T]_0 \ln(1 - P)} \qquad (4.1)$$

Dp is the number average degree of polymerisation, $[M]_0$, $[I]_0$ and $[T]_0$ are the initial concentrations of monomer, initiator and transfer agent. P is the conversion. *f* is the initiator efficiency. F_C is the fraction of termination that occurs by combination and K_{dt} is the rate of decomposition of initiator.

Topping *et al* have used equation 4.1 to determine the chain-transfer co-efficient for systems containing methyl methacrylate macromonomer with methyl

methacrylate monomer [12]. To determine accurately the chain transfer co-efficient each polymerisation was terminated at a low degree of conversion (Conversion<10%). The co-polymerisation reactions performed in this thesis are subject to several factors that contribute significantly to the degree of error incurred for the calculation of Cs. All reactions have been performed to give a high degree of conversion and all molecular weight data is obtained from GPC analysis calibrated with narrow PMMA standards. The determination of the Cs by either the Mayo equation (1.7) or from equation (4.1) is therefore subject to a large degree of error.

Chapter 2 described the synthesis of a range of PDMAEMA macromonomers and PMAA macromonomers from CCT mediated polymerisation. This chapter describes the co-polymerisation of these macromonomers with various acrylic co-monomers. The value of the Cs for these reactions is not determined since the large degree of error involved does not permit a quantitative comparison to be made. A plot of molecular weight versus the relative concentration of macromonomer added provides a qualitative measure of the degree of chain transfer that is taking place and allows elucidation of the mechanism of co-polymerisation. All water-soluble products from these reactions were tested for their dye-binding ability (Chapter 7).

4.1 RESULTS AND DISCUSSION

An initial series of tests to determine the efficacy for the co-polymerisation of PDMAEMA macromonomer with benzyl methacrylate and benzyl acrylate were performed.

4.1.1 Co-polymerisation of PDMAEMA macromonomer (Mn = 1100) with benzyl methacrylate (BzMA)

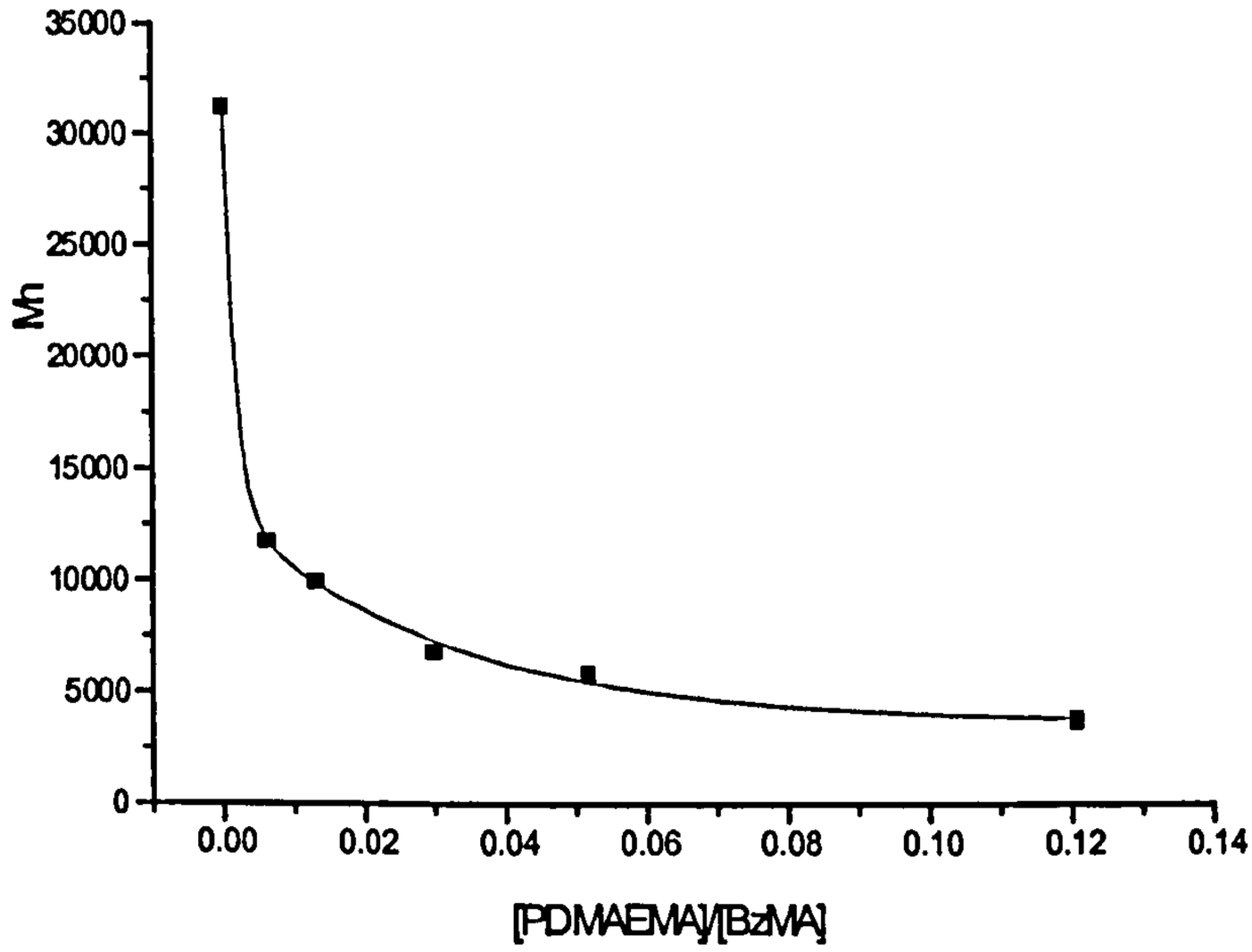
Co-polymerisation of BzMA with PDMAEMA macromonomer (Mn = 1100) was performed in toluene solution. Each reaction was performed with 10%

weight of total solids in solution at 70 °C for 14 hours. All reactions were initiated with 0.5 % weight AIBN with respect to monomer. Table 4.0 lists the relative concentrations used for each reaction and the molecular weight data determined for each product from THF GPC. One reaction was performed as a control where no PDMAEMA macromonomer was added. Conversion data is given based on gravimetry for each reaction performed.

Table 4.0 Experimental Data for the solution co-polymerisation of BzMA with PDMAEMA macromonomer (Mn = 1100) in toluene at 70 °C

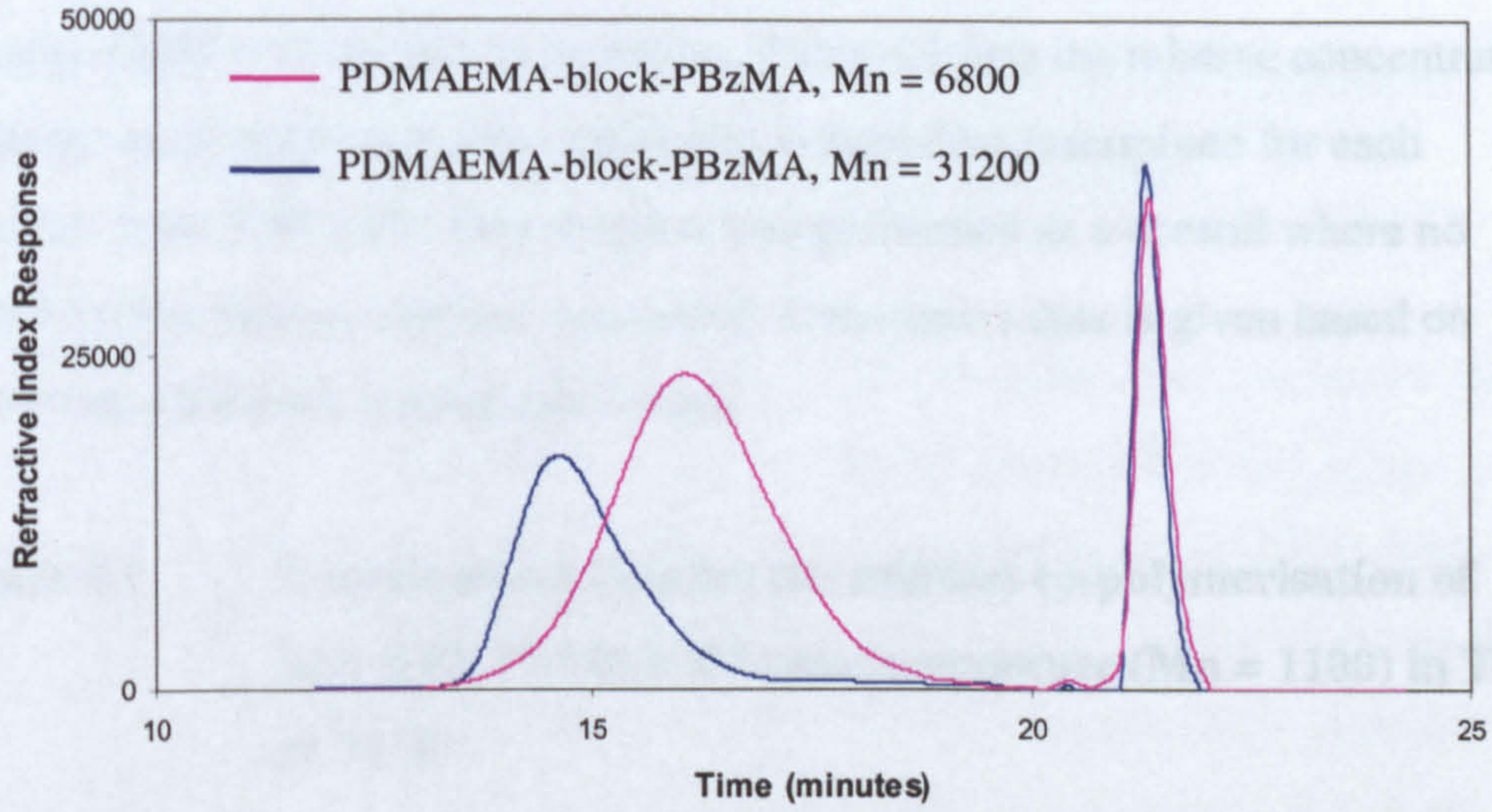
BzMA (g)	AIBN (mg)	[PDMAEMA]/ [BzMA] (molar ratio)10^{-3}	Mn	PDi	Conversion %
2.00	10.0	-	31200	1.88	100
2.13	10.6	6.34	11700	2.74	98
2.02	10.1	13.38	9900	1.84	94
1.79	9.0	30.08	6800	3.16	86
1.57	7.9	51.86	5800	3.00	74
1.12	6.6	120.95	3700	2.74	61

Figure 4.4 Plot of Mn vs co-monomer ratio for the polymerisation of BzMA in the presence of PDMAEMA macromonomer for 14 hours at 70 °C



Analysis of the product by GPC was used to determine the molecular weight distribution.

Figure 4.5 GPC of PDMAEMA-block-PBzMA co-polymer products in THF eluent



The refractive index response from the GPC of the products shows that a low molecular weight polymer with a unimodal distribution is formed. A degree of tailing to low molecular weight is observed.

A reduction in the average molecular weight of the co-polymer is observed as the percentage of macromonomer is increased [13]. The consumption of macromonomer and the reduction in the molecular weight of the co-polymer when compared with the homopolymer is attributed to the macromonomer acting as a chain transfer agent.

4.1.2 Co-polymerisation of PDMAEMA macromonomer (Mn = 1100) with benzyl acrylate (BzA)

Co-polymerisation of BzA with PDMAEMA macromonomer (Mn = 1100) was performed in toluene solution. Each reaction was performed with 10 % weight of total solids at 70 °C for 14 hours. All reactions were initiated with 0.5 % weight AIBN with respect to monomer. Table 4.1 lists the relative concentration used for each reaction and the molecular weight data determined for each product from THF GPC. One reaction was performed as a control where no PDMAEMA macromonomer was added. Conversion data is given based on gravimetry for each reaction performed.

Table 4.1 Experimental data for the solution co-polymerisation of BzA with PDMAEMA macromonomer (Mn = 1100) in THF at 70 °C

BzA (g)	AIBN (mg)	[PDMAEMA]/ [BzA] $x10^{-3}$	Mn	PDi	Conversion %
2.00	10.6	-	1 900	1.67	100
1.96	9.8	6.41	1 700	1.71	100
1.86	9.3	13.39	1 700	1.69	100
1.65	8.3	30.26	1 900	1.64	100
1.44	7.2	51.91	1 800	1.66	100
1.03	5.2	120.16	1 600	1.57	100

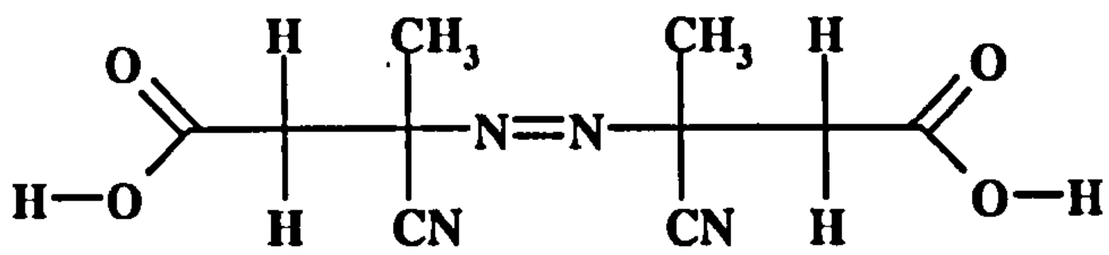
The data show that, for the homopolymerisation of BzA where no macromonomer is added, the molecular weight of the product that is formed is very low, this is in part due to the relatively high initiator concentration. No significant change in the degree of conversion, molecular weight distribution or polydispersity index is observed with the addition of macromonomer. The

homopolymerisation of BzA produces low molecular weight product, Mn = 1900 with complete conversion of monomer. This low molecular weight is indicative of a very high radical flux and a high degree of termination. Where the rate of graft formation, K_G, is fast then the molecular weight of the product will increase with increasing macromonomer content. The data indicate that k_g is low and that no significant graft formation has occurred.

4.1.3 Co-polymerisation of PDMAEMA macromonomer (Mn = 1100) with methacrylic acid (MAA)

Co-polymerisation of methacrylic acid with PDMAEMA macromonomer (Mn = 1100) was performed in aqueous solution. The reactions performed were analogous to those in section 4.1.1 for the co-polymerisation of BzMA with PDMAEMA macromonomer. Each reaction was performed with 50 % weight of total solids at 70 °C for 2 hours. The water-soluble initiator 4,4'-azobis(4-cyanovaleric acid) (CVA) (**4.1**) was used for each reaction with 1 % weight added with respect to monomer.

Figure 4.6 **4,4'-azobis(4-cyanovaleric acid) (CVA) (4.1)**



CVA (**4.1**)

Table 4.2 lists the relative concentrations used for each reaction and the molecular weight data determined for each product from THF GPC. One reaction was performed as a control where no PDMAEMA macromonomer was added. Conversion data is given based on gravimetry for each reaction performed.

The homopolymerisation of methacrylic acid remained homogeneous throughout the reaction. The co-polymerisations containing macromonomer

formed a gel during polymerisation, those containing higher concentrations of macromonomer gelled more quickly and produced a more viscous product.

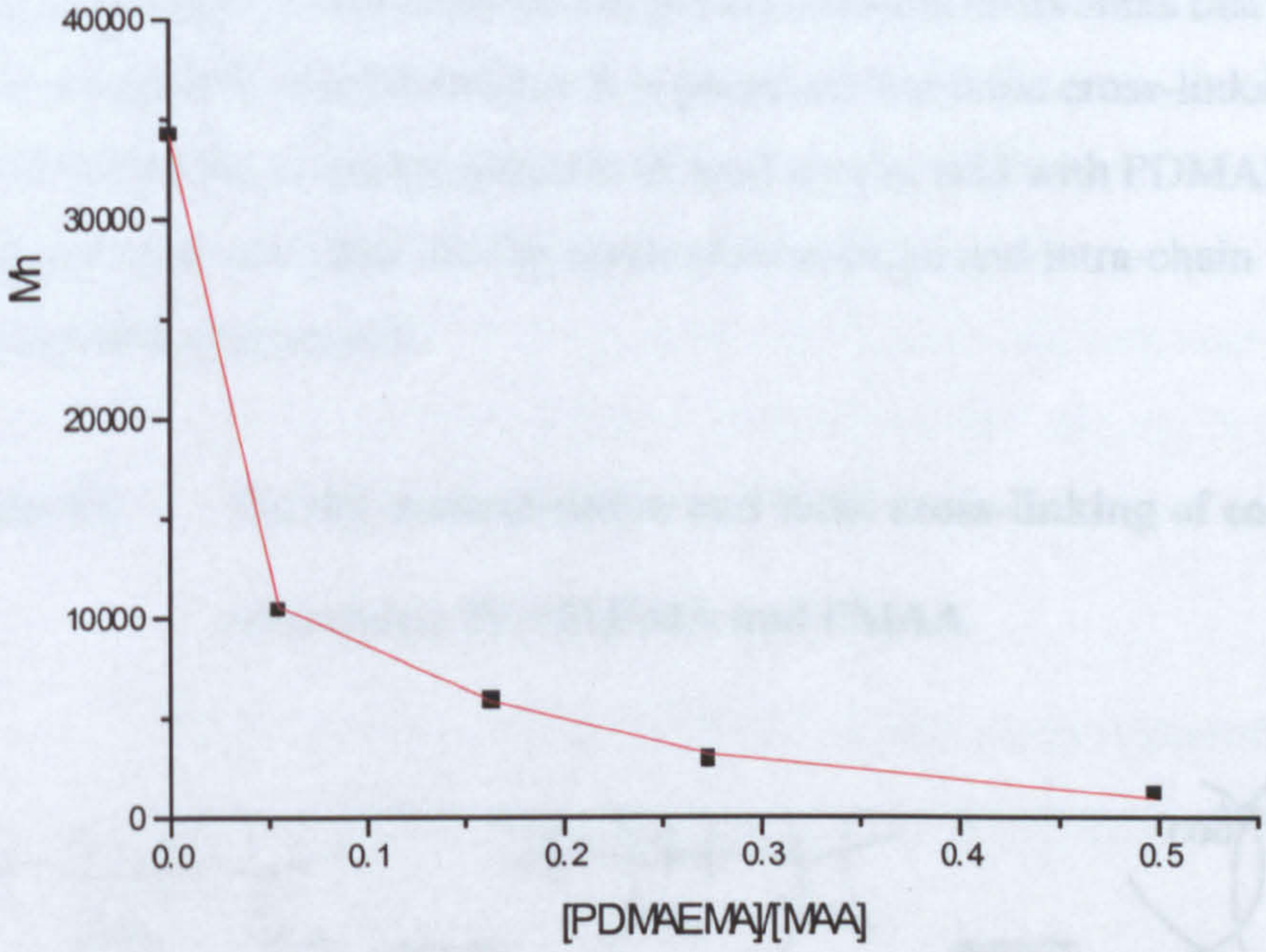
The co-polymer products were dissolved with the addition of potassium hydroxide pellets. The resulting solutions were precipitated into ice-cold acetone and neutralised with hydrochloric acid. Molecular weight data was obtained from the aqueous GPC of the products.

Table 4.2 Experimental data for the solution co-polymerisation of MAA with PDMAEMA macromonomer (Mn = 1100) in H_2O at 70 °C

MAA (g)	CVA (mg)	[PDMAEMA]/ [MAA] $x10^{-3}$	Mn[a]	PDi[a]	Conversion %
20.0	200.0	-	34 200	5.21	100
20.0	220.0	54.8	10 400	3.13	100
6.7	86.0	163.5	5 900	2.74	85
4.0	60.0	273.8	2 900	2.35	64
2.2	42.0	497.8	1 200	2.57	39

[a] Molecular weight data obtained from aqueous GPC calibrated with narrow PEG standards. The eluent used was ultra pure water at pH 10 (TRIZMA buffer) and 0.5 M NaCl.

Figure 4.7 **Plot of molecular weight of co-polymer product prepared from PDMAEMA (Mn =1100) versus relative macromonomer concentration [PDMAEMA]/[MAA]**

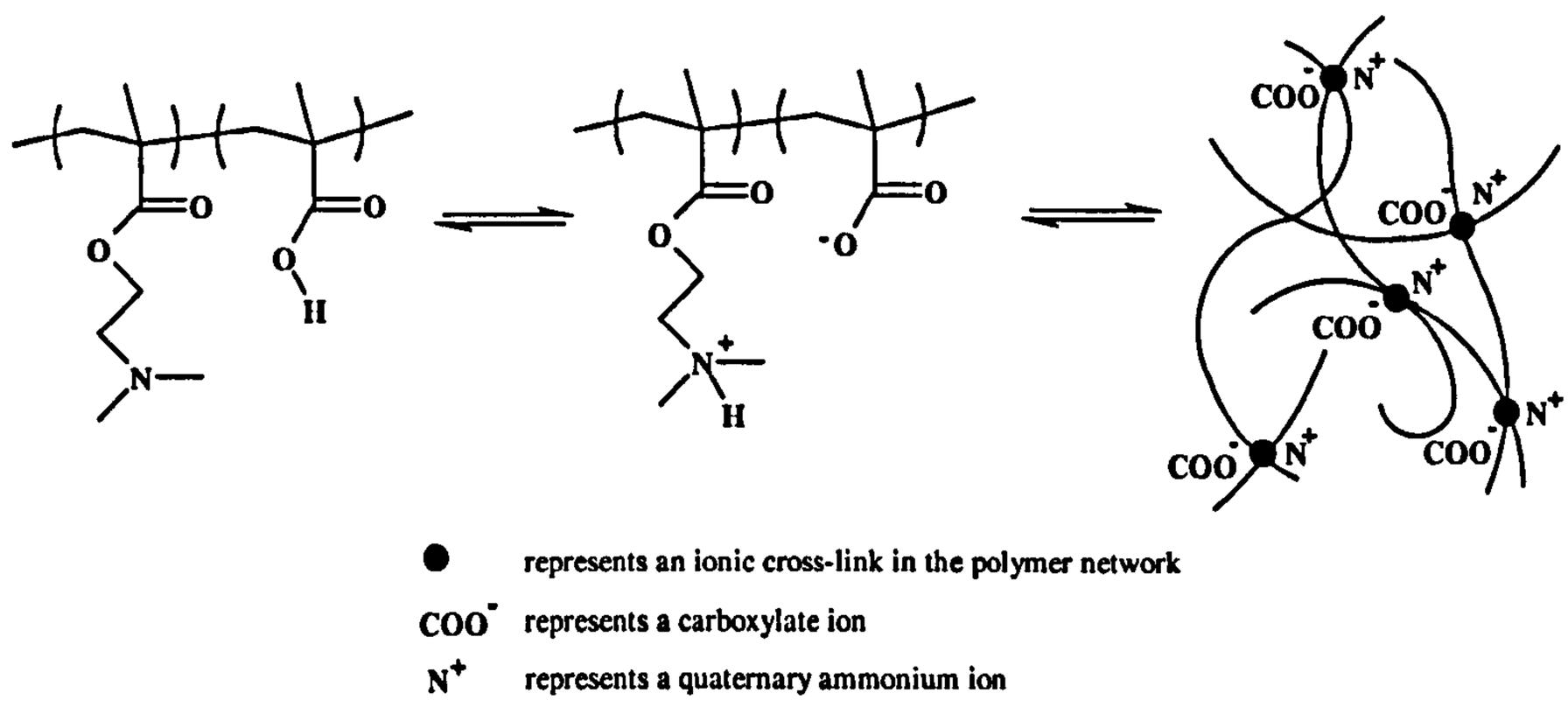


NMR analysis of the co-polymer products was difficult to perform due to gelation of the product in D_2O. The addition of potassium hydroxide pellets was used to solubilise the product. However, excessive peak broadening and concentration dependent shifts in the ^1H NMR prevented elucidation of the co-monomer composition and structure.

The observed gelation of the co-polymer product during polymerisation is believed to result from the formation of an ionic water absorbent network [14,15]. Cross-linked partially neutralised poly(acrylic acid) and other poly(ionic) networks have been reported to be excellent water absorbers ("superabsorbers") [16,17]. The anionic carboxylate groups present in neutralised poly(acrylic acid) increase solvation due to large ion-dipole interactions. Coulombic interactions in the polymer backbone stiffen the polymer chain and this results in an increase in the hydrodynamic volume of the polymer. Counter ions are solvated into the system and this results in an increase in the swelling of the chain. Water is absorbed into the interior of the network to minimise the energy of the system.

As water diffuses into the network the volume is increased and swelling of the network takes place. The cross-linked network is solvated by the water yet remains insoluble due to the degree of cross-linking present and produces a swollen gel. Typically acrylic acid is co-polymerised with a cross-linking agent such as allyl methacrylate to form a covalent cross-link [16]. The co-polymer products obtained in this study do not posses covalent cross-links that are found in many industrial superabsorbers. It is proposed that ionic cross-links are formed during the co-polymerisation of methacrylic acid with PDMAEMA macromonomer and these are the result of inter-chain and intra-chain neutralisation (Figure 4.8).

Figure 4.8 Partial neutralisation and ionic cross-linking of co-polymer containing PDMAEMA and PMAA



The carboxylate groups and the quaternary amine groups can form ionic cross-links between polymer chains and form a network structure. As the molar ratio of amine and acid residues in the reaction mixture becomes closer to unity then the degree of neutralisation and the resulting degree of cross-linking will increase. As the degree of cross-linking increases then the more viscous the gel will become. An increase in viscosity was observed for all reactions as the proportion of macromonomer was increased. The addition of concentrated base to the aqueous polymer gel produces the salt of the acrylic acid and deprotonates the quaternary amine groups and this results in the collapse of the cross-linked network.

The homopolymer of methacrylic acid that was formed did not show gelation, this is expected since no neutralisation or cross-linking had occurred and therefore the product is readily soluble in water.

An increase in the relative concentration of the PDMAEMA macromonomer resulted in a decrease in the molecular weight of the product, indicating that chain-transfer had occurred leading to block co-polymer formation. The low conversion achieved for reactions containing greater concentrations of macromonomer with respect to methacrylic acid is due to increased chain-transfer reducing the rate of co-polymerisation. Conversion may also be reduced as a result of monomer trapping from increased solution viscosity as a result of cross-linking.

4.1.4 Co-polymerisation of PDMAEMA macromonomer (Mn = 4200) with methacrylic acid (MAA)

Co-polymerisation of methacrylic acid with PDMAEMA macromonomer (Mn = 4200) was performed in aqueous solution. These reactions are directly analogous to those in Section 4.1.3 for the co-polymerisation of PDMAEMA macromonomer (Mn = 1100) with MAA. Each reaction was performed with 50 % weight of total solids at 70 °C for 2 hours. The water-soluble initiator 4,4'-azobis(4-cyanovaleric acid) (CVA) (**4.1**) was used for each reaction with 1 % weight added with respect to monomer. Table 4.3 lists the relative concentrations used for each reaction and the molecular weight data determined for each product from THF GPC. One reaction was performed as a control where no PDMAEMA macromonomer was added. Conversion data is given based on gravimetry for each reaction performed.

The co-polymerisations containing macromonomer formed a gel during polymerisation, those containing higher concentrations of macromonomer gelled more quickly and produced a more viscous product. The products were isolated and analysed using the methods outlined in section 4.2.3.

Table 4.3 Experimental Data for the solution co-polymerisation of MAA with PDMAEMA macromonomer (Mn = 4200) in H_2O at 70 °C

MAA (g)	CVA (mg)	[PDMAEMA]/ [MAA] (molar ratio) x10^{-3}	Mn[a]	PDi[a]	Conversion %
20.0	200.0	-	34 200	5.21	100
3.3	53.0	165.9	3 700	8.34	92
2.0	40.0	273.8	3 400	6.02	83
1.4	34.0	391.1	2 400	5.86	51
1.1	31.0	497.8	2 400	3.67	27

[a] Molecular weight data obtained from aqueous GPC calibrated with narrow PEG standards. The eluent used was ultra pure water at pH 10 (TRIZMA buffer) and 0.5 % NaCl.

The data show that for the co-polymerisation products from PDMAEMA macromonomers (Mn = 1100 and Mn = 4200) with methacrylic acid that molecular weight reduction is observed when compared with polymerisation of methacrylic acid excluding macromonomer. A comparison of the product co-polymer molecular weight data showed that, for analogous reactions of macromonomer with methacrylic acid, the lower molecular weight macromonomer (Mn = 1100) generally gave a larger reduction in molecular weight. No direct correlation between the observed molecular weight reduction from each series of reactions can be made due to differences in the respective concentrations of amine residues compared with acid residues in the reaction mixtures. All co-polymerisation reactions formed highly viscous gels, this is the result of ionic cross-linking of the co-polymer product.

4.1.5 Co-polymerisation of PDMAEMA macromonomer (Mn = 1100) with acrylic acid (AA)

Co-polymerisation of AA with PDMAEMA macromonomer (Mn = 1100) was performed in THF solution. Each reaction was performed with 50 % weight of total solids at 70 °C for 2 hours. All reactions were initiated with 1 % weight AIBN with respect to monomer. Table 4.4 lists the relative concentration used for each reaction and the molecular weight data determined for each product from THF GPC. One reaction was performed as a control where no PDMAEMA macromonomer was added. Conversion data is given based on gravimetry for each reaction performed.

The co-polymerisations containing macromonomer formed gels during polymerisation. The products were isolated and analysed using the methods outlined in sections 4.2.3.

Table 4.4 Experimental data for the solution co-polymerisation of AA with PDMAEMA macromonomer (Mn = 1100) in THF at 70 °C

AA (g)	AIBN (mg)	[PDMAEMA]/ [AA] (molar ratio) $x10^{-3}$	Mn[a]	PDi[a]	Conversion %
20.00	10.6	-	139 800	27	100
20.00	9.8	6.41	-	-	63
6.67	9.3	13.39	228 200	11	78
4.00	8.3	30.26	-	-	42
2.86	7.2	51.91	1 025 300	70	49
2.22	5.2	120.16	1 450 000	35	22

[a] Molecular weight data obtained from aqueous GPC calibrated with narrow PEG standards. The eluent used was ultra pure water at pH 10 (TRIZMA buffer) and 0.5 % NaCl.

The analysis of these products was difficult to perform and precluded interpretation of the reaction products. The GPC analysis showed peak broadening for all co-polymer samples and all chromatograms showed multi-modal distributions resulting in high polydispersity indicies. No trend in the degree of conversion, molecular weight distribution or polydispersity index was observed with the addition of macromonomer. The homopolymerisation of AA gave high molecular weight product, Mn > 100000 with complete conversion of monomer. No evidence for graft formation was observed for the polymerisation of acrylic acid with PDMAEMA macromonomer.

4.1.6 Co-polymerisation of PMAA macromonomers with DMAEMA

Aqueous solution co-polymerisation of PMAA macromonomer was attempted with DMAEMA monomer, however no co-polymer products were obtained. A series of experiments analogous to those performed for PDMAEMA macromonomer with BzMA (section 6.2.1) were performed. From NMR analysis all reactions showed that no PDMAEMA was present in the product. A recent paper by van der Wetering *et al* outlined the hydrolytic instability of the DMAEMA monomer [18]. The DMAEMA monomer undergoes base catalysed hydrolysis in water to form methacrylic acid, the rate of hydrolysis increases at elevated temperatures.

4.2 CONCLUSION

Co-polymerisation of PDMAEMA macromonomer with BzMA and with MAA was performed and evidence for block-copolymer formation was obtained from

the GPC of the products. No evidence for graft co-polymerisation of BzA or AA with PDMAEMA macromonomer was observed.

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Chapter 5

ATOM TRANSFER POLYMERISATION (ATP)

Curiosity

has its own reason

for exsiting.

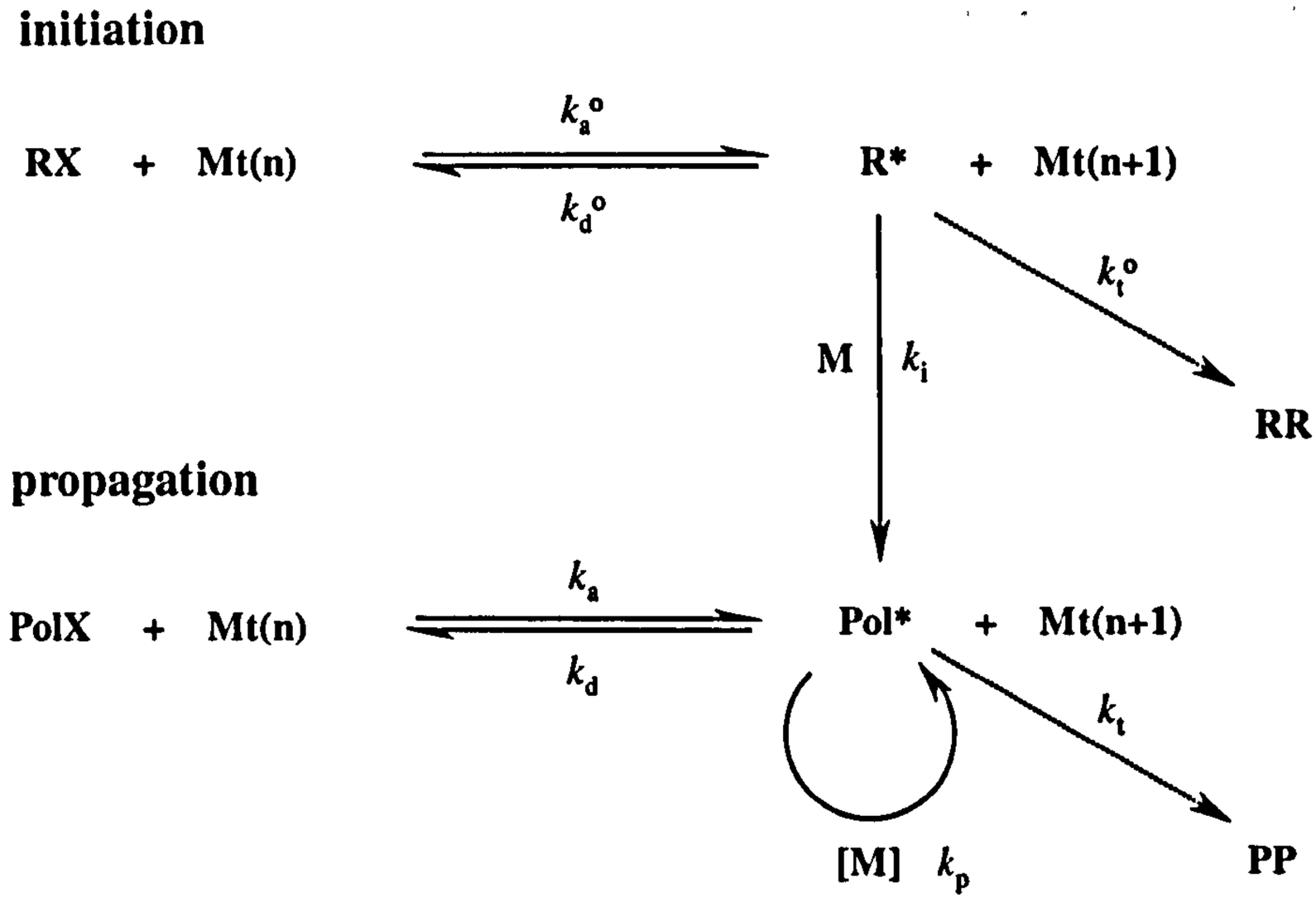
Albert Einstein

5.0 INTRODUCTION

A general review of Atom Transfer Polymerisation (ATP) was given in Chapter 1 section 1.5.1.2. This section will introduce the specific details for the ATP methods used in this body of research.

Atom Transfer polymerisation is based on the reversible reaction between a transition metal complex and a dormant alkyl halide species. Reversible homolysis of the dormant alkyl halide molecule produces a propagating radical that acts as an active species for polymerisation [1]. The halogen atom is transferred to the transition metal complex [2-4]. The nature of the transition metal complex employed mediates the position of equilibrium between the dormant and active species. Figure 5.0 illustrates a kinetic representation of ATP for a generic system.

Figure 5.0 Atom Transfer Polymerisation (ATP)



RX and Mt represent the alkyl halide initiator and the metal catalyst. n is the formal oxidation state of the metal complex. R* and Pol* represent the activated initiating species and the activated propagating polymer chain. Pol-X represents the dormant alkyl halide species. M is monomer and RR and PP represent two forms of primary radical termination products. k_a^o and k_a are the rates of

activation for the initiator species and the dormant polymer species. k_d^o and k_d are the rates of deactivation for the activated initiator species and the activated polymer chain. k_t^o and k_t are the rates of primary radical-radical termination for the activated initiator species and the activated polymer chain. k_i is the rate constant for initiation of the activated initiator species with monomer and k_p is the rate constant for propagation of the activated polymer chain with monomer.

The following expression for the rate of polymerisation has been derived in the literature based on the mechanism outlined in figure 5.0 [5]. The rate of polymerisation is also given in terms of the apparent rate of reaction (k_p^{app}) with respect to monomer [M].

$$R_p = k_p\left(\frac{k_a}{k_d}\right)[M][RX]_0\left(\frac{[Mt(n)]}{[Mt(n+1)}\right) = k_P{}^{app}[M] \qquad \textbf{(5.0)}$$

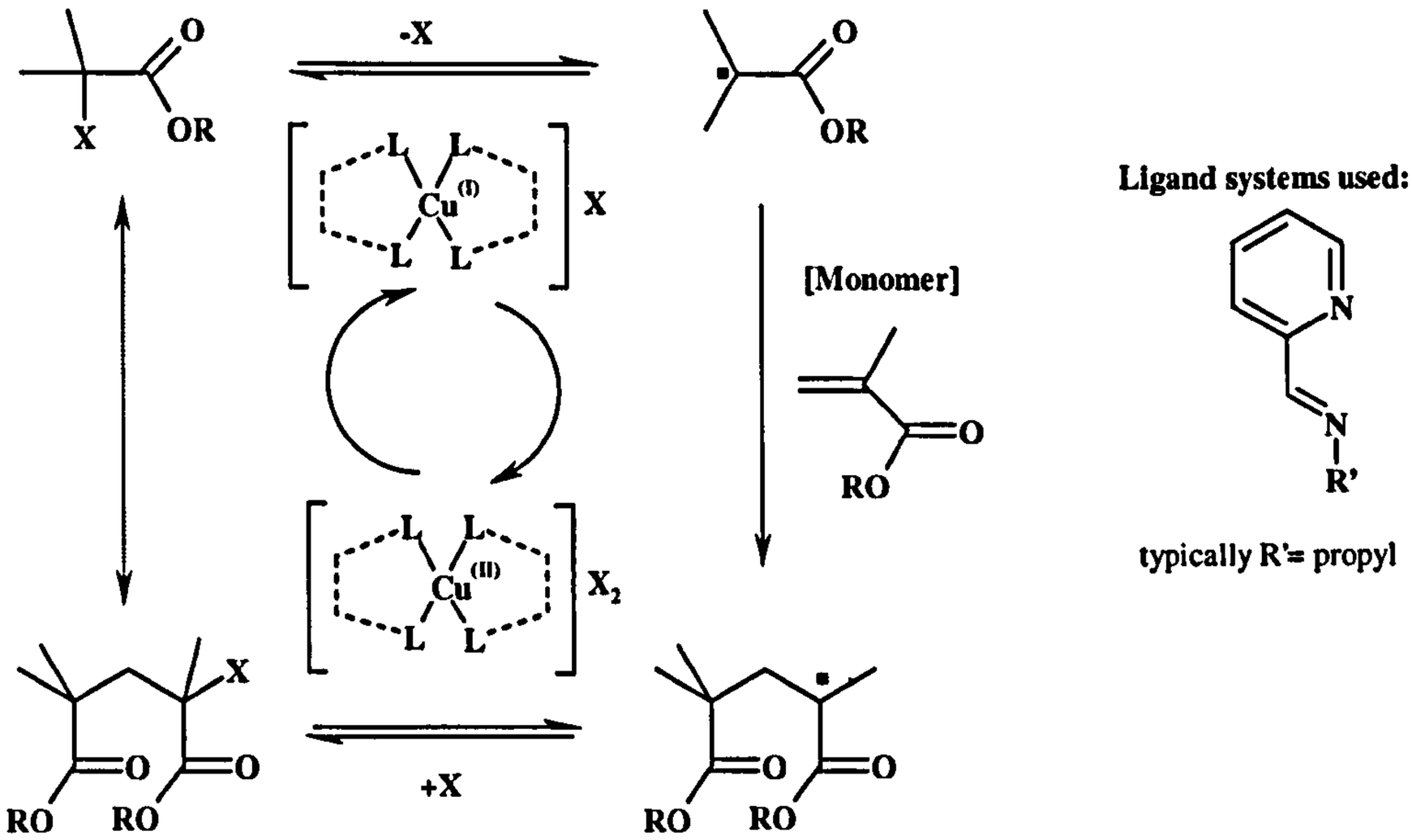
The rate of propagation is first-order with respect to the active polymer species (Pol*) and the rate of termination is second order, therefore at low concentrations of active species the degree of termination is reduced in comparison to the rate of propagation. Living polymerisation is achieved when equilibrium is established such that the majority of chains are present in the dormant state. The concentration of propagating radicals is reduced and this consequently inhibits irreversible termination reactions due to combination and disproportionation. For living polymerisation the molecular weight increases linearly with reaction time.

Sawamoto *et al* introduced a homogeneous system based on a $Ru(II)Cl_2(PPh_3)_3$ catalyst and Matyjaszewski and co-workers introduced a homogeneous system based on a system comprising Cu(I)Cl together with two 2,2'-bipyridine (bpy) ligands [6-10]. Rh(III) [11], Pd(II) [12] and Ni(II) [13,14] complexes were shown to provide controlled polymerisation of methacrylates and the copper bipyridyl complex was shown to provide controlled polymerisation of styrene and acrylates.

Research into ATP has concentrated on the development of cheaper universal systems that allow for the controlled polymerisation of a range of monomer types in different solvents. Matyjaszewski and Haddleton have both developed systems that allow for the controlled polymerisation of methacrylate monomers with various metal and ligand species [10,15-17]. Haddleton *et al* developed a series of Schiff base ligands that are simple to prepare in quantitative yields and which provide controlled polymerisation of methacrylate monomers when used in conjunction with copper(I) halides [16]. At present the use of ATP for industrial applications is limited due to the emerging nature of the chemistry and the necessity for the removal of the catalyst from the product polymer. Catalyst can be removed from the polymer by passing the product through basic alumina and by precipitating the polymer into a non-solvent; however these methods restrict the catalyst to being used only once. Haddleton *et al* have demonstrated the use of heterogeneous catalysis with solid supported Schiff base ligands on polystyrene/silica beads for ATP that facilitate the easy removal and reuse of the catalyst species [18,19]. The product polymer from these systems does not require any further purification to remove catalyst. However, a small increase in the polydispersity index is observed in comparison to homogeneous systems.

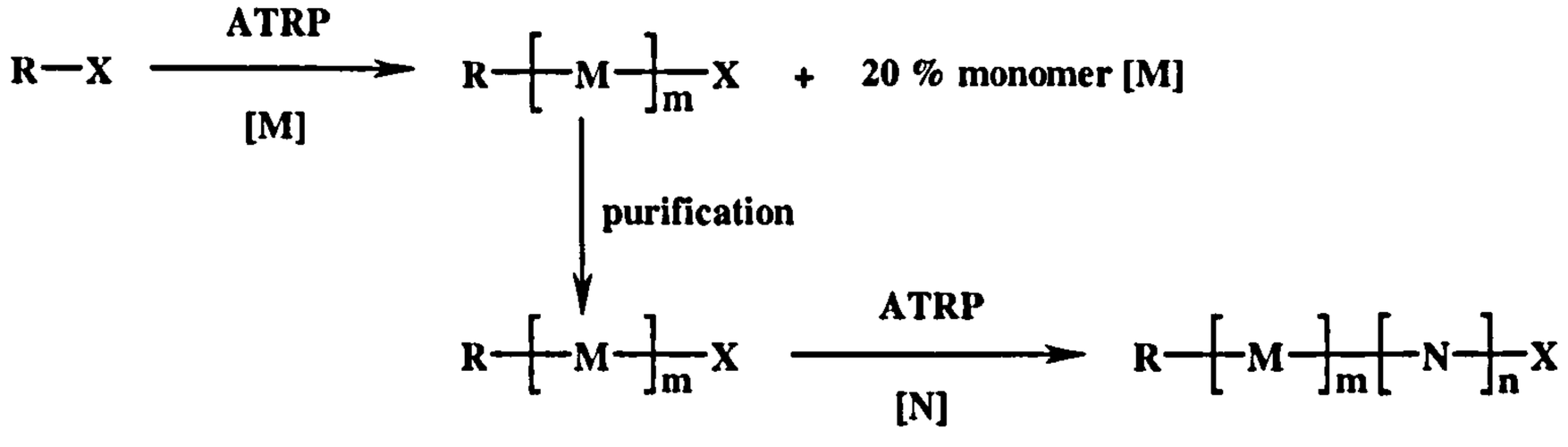
Research has also focused on the elucidation of the mechanism of ATP [5]. The propagation step is believed to take place by either a traditional free radial process or by a more complicated concerted pathway, no absolute proof for either pathway has been reported. For the purpose of clarity, a free-radical mechanism is outlined in Figure 5.1, which represents the polymerisation of a methacrylate monomer using a copper(I) halide in conjunction with a generic Schiff base ligand N-(alkyl)-2-pyridylmethanimine.

Figure 5.1 **Atom Transfer Polymerisation of methacrylate with copper(I) halide in conjunction with N-(alkyl)-2-pyridylmethanimine ligands**



Where the rate of termination is zero then every chain in the product polymer from ATP will contain terminal alkyl halide functionality. This alkyl halide functionality is analogous to the initiator species and therefore the product polymer can act as a macro-initiator for subsequent block co-polymer synthesis. For ideal block co-polymers all chains in the macro-initiator should contain terminal alkyl halide functionality. At high degrees of conversion the rate of termination increases and therefore the percentage of polymer chains that contain alkyl halide functionality is reduced, this manifests itself as a degree of homopolymer impurity after co-polymerisation. In practice, polymerisation of a monomer to produce a macro-initiator is usually stopped at less than 80 % of monomer consumption to ensure that the number of chains that are terminated by alkyl halide functionality is optimised [20,21]. The macro-initiator is then purified and used to initiate polymerisation with a second monomer. Figure 5.2 outlines the process for block co-polymer formation.

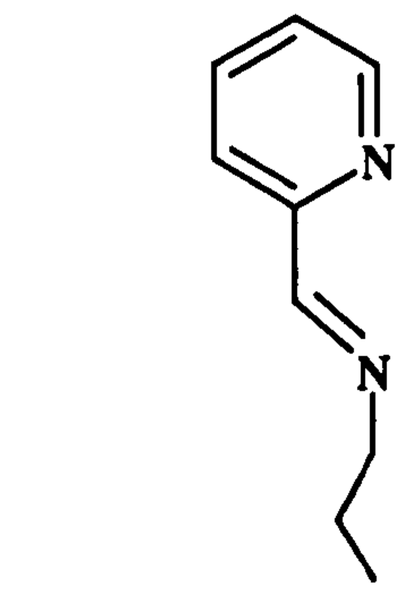
Figure 5.2 Block co-polymer synthesis from ATP



The syntheses of a variety of different functional block, gradient and hyperbrached products have been reported [22,23], a number of which contain amine functional monomers e.g., DMAEMA. Where the block co-polymer contains an amine functional monomer then in all cases the amine functional monomer is polymerised from a macro-initiator [24,25].

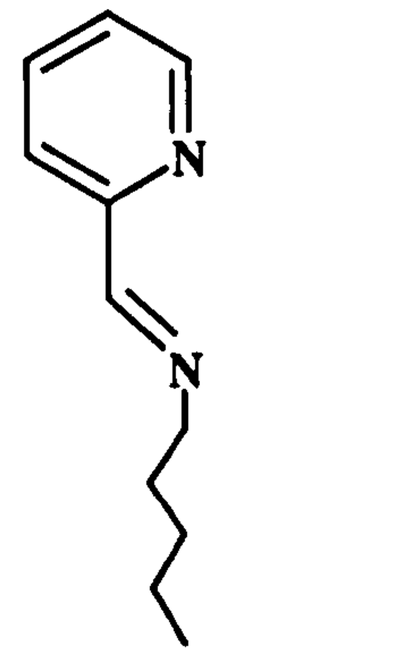
The N-(alkyl)-2-pyridylmethanimine type ligands developed by Haddleton *et al* that have predominately been used are N-(n-pentyl)-2-pyridylmethanimine and N-(propyl)-2-pyridylmethanimine together with copper(I) bromide. The initiator that has predominantly been used is ethyl-2-bromoisobutyrate.

Figure 5.3 Ligands and initiators used for atom transfer polymerisation



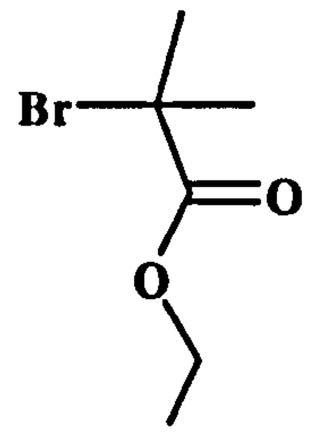
N-(propyl)-2-pyridylmethanimine ligand

(5.1)



N-(n-pentyl)-2-pyridylmethanimine ligand

(5.2)



ethyl-2-bromoisobutyrate initiator

(5.3)

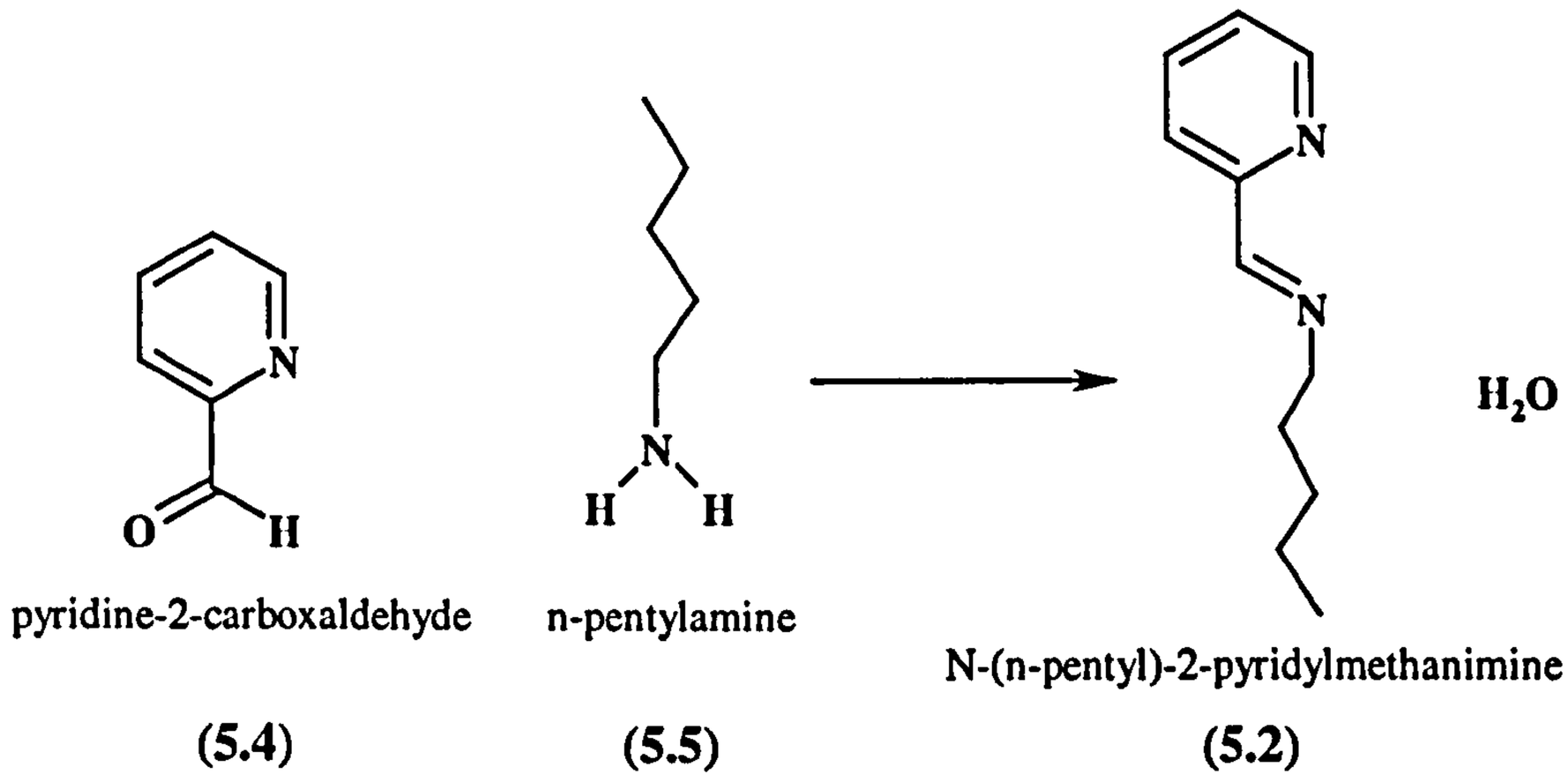
This chapter will outline the synthesis of a range of block co-polymer species from ATP where both blocks contain amine functionality, where one block can be selectively quaternised to produce a block co-polymer that contains one tertiary amine block and one quaternary amine block. These block co-polymer products are analogous in monomer composition to those statistically quaternised co-polymers whose synthesis was outlined in Chapter 2. Analysis of the dye-binding ability of these block co-polymer species in comparison to the statistical polymers can then be used to determine whether the conformation of the polymer influences the dye-binding ability.

5.1 RESULTS AND DISCUSSION

5.1.1 Reagents

The ligand that has been predominately used in this body of research is N-(n-pentyl)-2-pyridylmethanimine (**5.2**) together with copper(I) bromide. The N-(n-pentyl)-2-pyridylmethanimine ligand (**5.2**) was synthesised in quantitative yield and was purified by vacuum distillation [16,26,27].

Figure 5.4 Synthesis of N-(n-pentyl)-2-pyridylmethanimine (5.6) ligands



pyridine-2-carboxaldehyde (5.4)

n-pentylamine (5.5)

N-(n-pentyl)-2-pyridylmethanimine (5.2)

The Cu(I) Br was purified using the method of Keller and Wycoff [28].

5.1.2 Atom Transfer Polymerisation of methyl methacrylate (MMA) in toluene at 90 °C

The polymerisation of methyl methacrylate by atom transfer polymerisation mediated using Cu(I)Br with N-(pentyl)-2-pyridylmethanimine ligands has been previously reported in the literature [26,29]. A series of atom transfer polymerisations of MMA were performed to determine the apparent rate of reaction (k_p^{app}) for the system. A comparison of this data can then be made with all subsequent polymerisations of different monomers and solvents.

Unless otherwise stated, standard Schlenk techniques and syringe transfer techniques were made in an atmosphere of dry nitrogen, as outlined in the experimental section.

The monomer used in each case was MMA, the initiator used for all reactions was ethyl-2-bromoisobutyrate (**5.3**) and the ligand used for each reaction was N-(n-pentyl)-2-pyridylmethanimine (n-pentyl) (**5.2**). For each reaction the monomer [M], initiator [I], [copper(I) bromide] and ligand [L] concentrations are given in terms of their molar ratio. A series of different monomer to initiator concentrations were used to determine the effect on the kinetics for the reaction and the degree of control obtained. Each reaction was performed in toluene solution with 33 % weight solids at 90 °C for 5 hours. Table 5.0 lists the different reaction conditions used for each polymerisation. These are similar conditions to those outlined by Haddleton *et al* [16].

Table 5.0 Reaction conditions for the Atom Transfer Polymerisation of MMA in toluene at 90 °C

		Molar ratio			
MMA (g)	**Toluene (g)**	**Monomer [M]** MMA	**Initiator [I]** Ethyl-2-bromoisobutyrate	**[Cu(I)Br]**	**Ligand [L]** n-pentyl
20	40	100	1	1	2
20	40	100	2	1	2
20	40	100	3	1	2

Table 5.1 lists the molecular weight and conversion data obtained by gravimetry from the extracts of the reaction where [Monomer]:[Initiator] = [100]:[2].

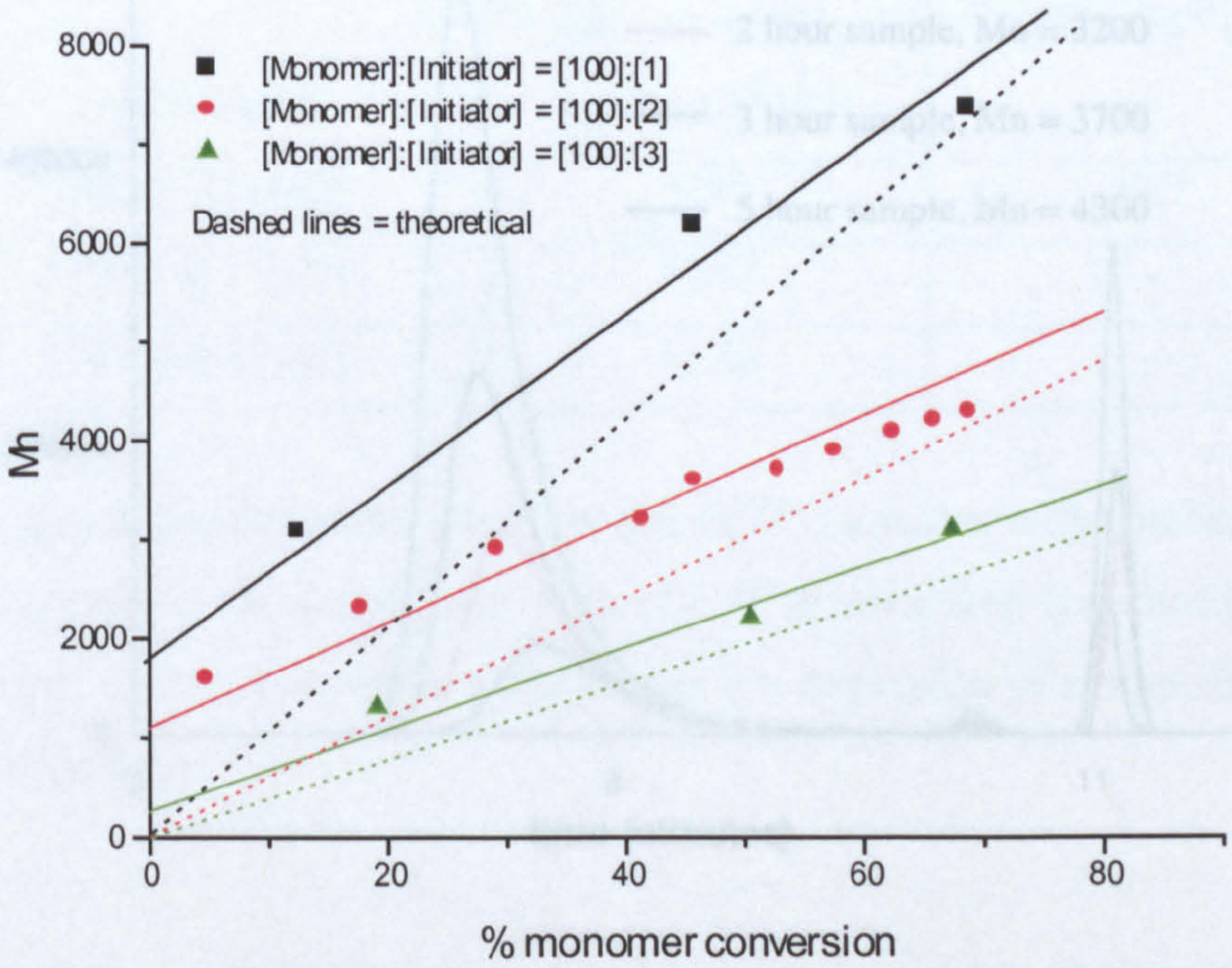
Table 5.1 Molecular weight and conversion data for ATP of MMA with [Monomer]:[Initiator] = [100]:[2] in toluene at 90 °C

Sample (hours)	**Mn**	**PDi**	**Conversion (%)**	**Theoretical Mn***
0.5	1600	1.29	4.7	400
1	2300	1.28	17.7	1100
1.5	2900	1.28	29.9	1700
2	3200	1.29	41.4	2300
2.5	3600	1.26	45.8	2500
3	3700	1.29	52.8	2800
3.5	3900	1.29	57.5	3000
4	4100	1.30	62.4	3300
4.5	4200	1.31	65.9	3500
5	4300	1.30	68.9	3600

* The theoretical Mn values are calculated using equation 1.8 from chapter 1 section 1.5.2.

The molecular weight data for the reactions containing [Monomer]:[Initiator] = [100]:[1], [100]:[2] and [100]:[3] are plotted as molecular weight versus % monomer conversion.

Figure 5.5 Plot of Mn versus % monomer conversion for the ATP of MMA in toluene at 90 ° C



The graph shows that molecular weight approximately increases linearly with % monomer conversion. The product polymers show an observed Mn higher than those predicted by theory based on the instantaneous conversion. The higher than expected Mn is more prominent at the beginning of the reaction, which indicates slow initiation relative to propagation or that a some initiator is lost through primary radical-radical termination pathways, thus reducing initiator efficiency. These observations have been previously reported for the ATP of MMA [5, 29].

Figure 5.6 shows the GPC overlay for a range of samples from the polymerisation of MMA by ATP. The chromatograms show that each polymer has a narrow unimodal distribution. For all reactions the products were near

monodisperse, (PDi<1.3) showing an excellent degree of control for the polymerisation process.

Figure 5.6 GPC overlay for the polymerisation of MMA by ATP in toluene at 90 °C with [Monomer]:[Initiator] = [100]:[2]

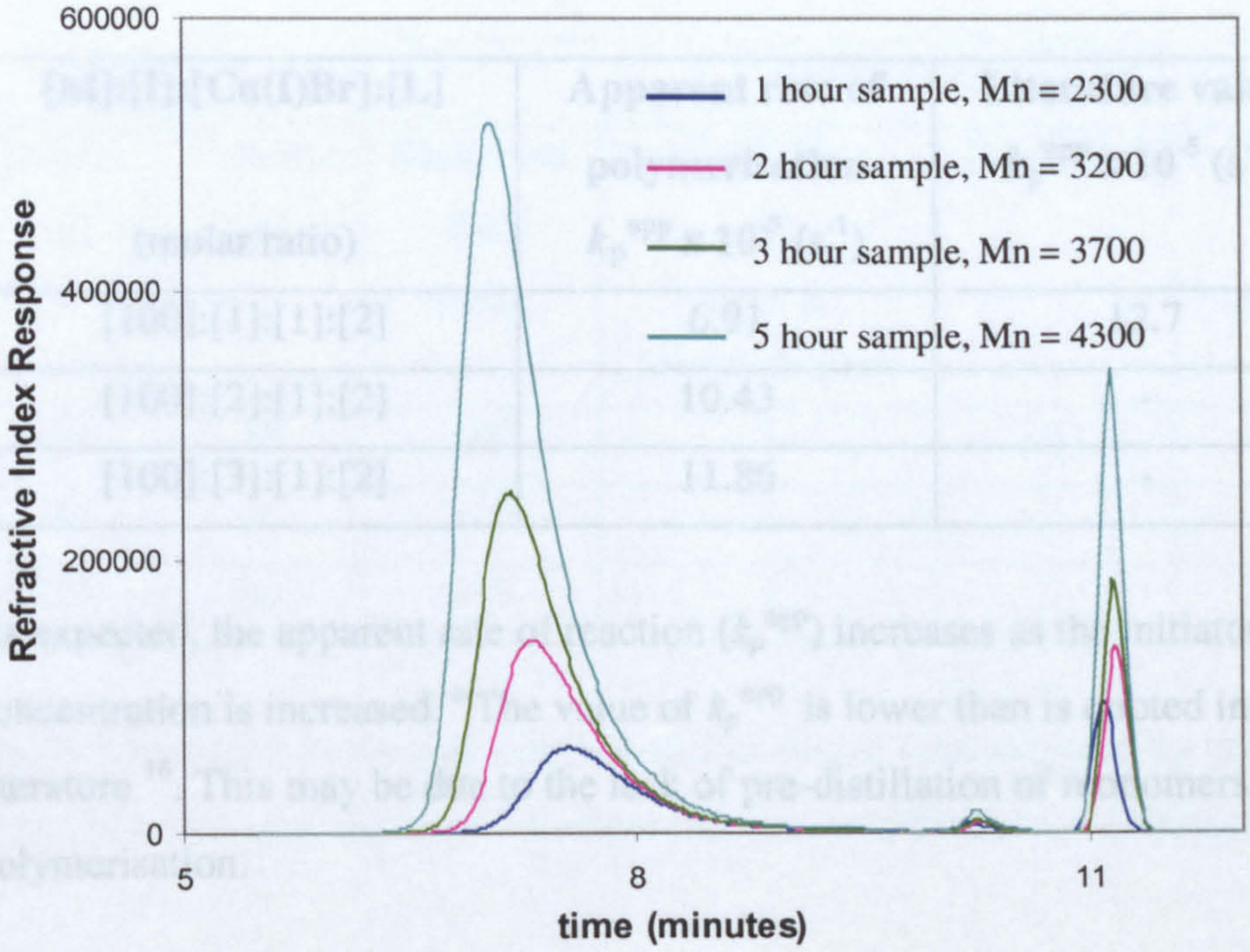
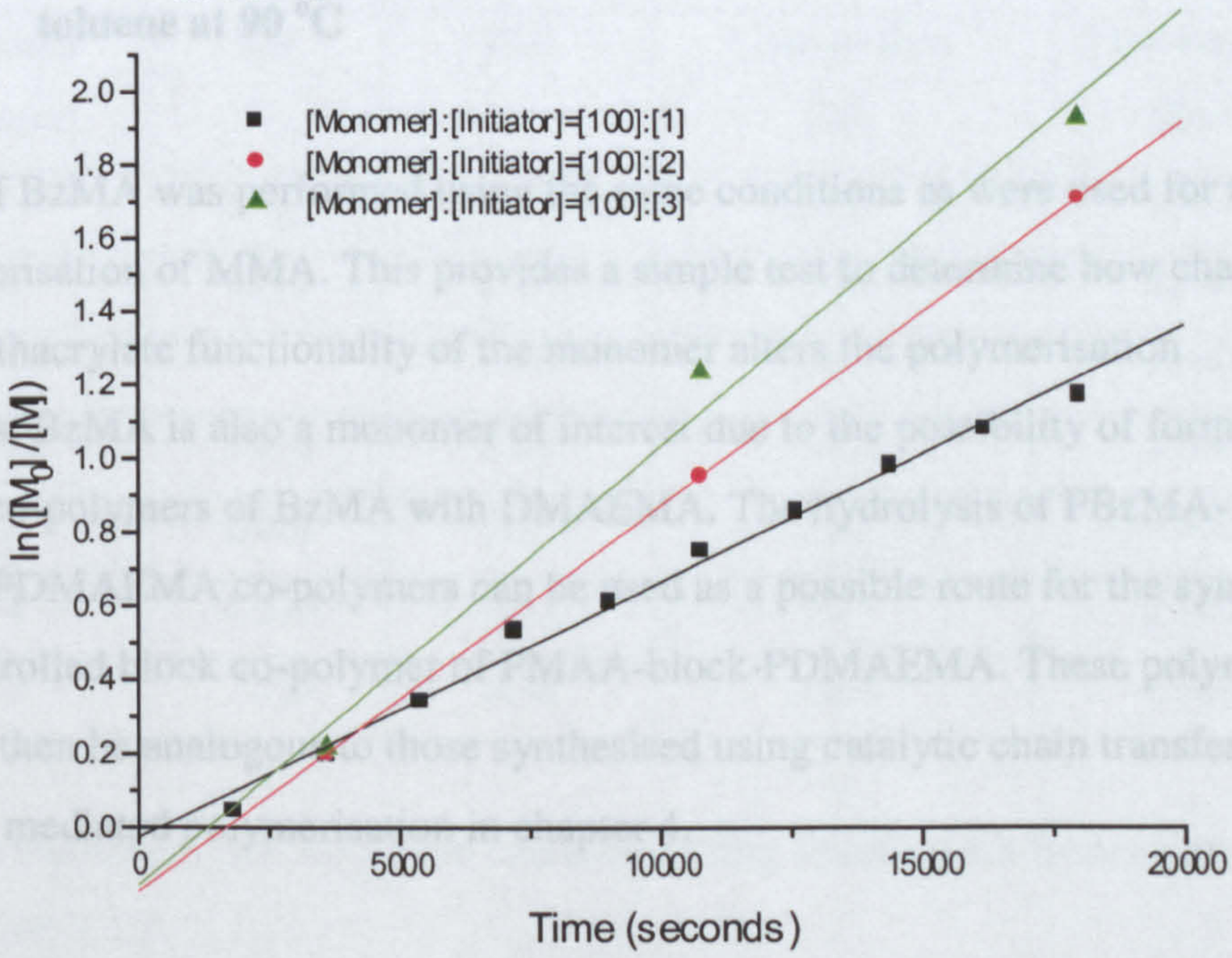


Figure 5.7 First-order kinetic rate plot for the ATP of MMA in toluene at 90 °C



The first-order rate plot is linear for all reactions, indicating that the number of active species remains constant throughout the polymerisation and that the rate of termination is minimal.

Table 5.2 Apparent rate of polymerisation for the ATP of MMA in toluene at 90 °C

[M]:[I]:[Cu(I)Br]:[L] (molar ratio)	Apparent rate of polymerisation k_p^{app} x 10^{-5} (s^{-1})	Literature value[a] k_p^{app} x 10^{-5} (s^{-1})
[100]:[1]:[1]:[2]	6.91	12.7
[100]:[2]:[1]:[2]	10.43	-
[100]:[3]:[1]:[2]	11.86	-

As expected, the apparent rate of reaction (k_p^{app}) increases as the initiator concentration is increased. [a] The value of k_p^{app} is lower than is quoted in the literature [16]. This may be due to the lack of pre-distillation of monomers before polymerisation.

5.1.3 Atom Transfer Polymerisation of benzyl methacrylaye (BzMA) in toluene at 90 °C

ATP of BzMA was performed using the same conditions as were used for the polymerisation of MMA. This provides a simple test to determine how changing the methacrylate functionality of the monomer alters the polymerisation process. BzMA is also a monomer of interest due to the possibility of forming block co-polymers of BzMA with DMAEMA. The hydrolysis of PBzMA-block-PDMAEMA co-polymers can be used as a possible route for the synthesis of controlled block co-polymer of PMAA-block-PDMAEMA. These polymers would then be analogous to those synthesised using catalytic chain transfer (CCT) mediated polymerisation in chapter 4.

Three polymerisations were performed with different [Monomer]:[Initiator] ratios. Table 5.3 outlines the reagent composition for each reaction performed.

Table 5.3 Reaction conditions for the Atom Transfer Polymerisation of BzMA in toluene at 90 °C

		Molar ratio			
BzMA (g)	**Toluene** (g)	**Monomer [M]** BzMA	**Initiator [I]** Ethyl-2-bromoisobutyrate	**[Cu(I)Br]**	**Ligand [L]** n-pentyl
20	40	100	1	1	2
20	40	100	2	1	2
20	40	100	3	1	2

Table 5.4 lists the molecular weight and conversion data obtained by gravimetry from the extracts of the reaction where [Monomer]:[Initiator] = [100]:[2].

Table 5.4 Molecular weight and conversion data for ATP of BzMA with [Monomer]:[Initiator] = [100]:[2] in toluene at 90 °C

Sample (hours)	**Mn**	**PDi**	**Conversion** (%)	**Theoretical Mn***
0.5	3200	1.37	9.6	1000
1	4300	1.36	24.2	2300
1.5	-	-	30.7	2900
2	5400	1.36	39.1	3700
3	6000	1.37	52.1	4800
4	6600	1.37	60.1	5500
5	7000	1.38	68.4	6200

* The theoretical Mn values are calculated using equation 1.8 from chapter 1 section 1.5.2.

The molecular weight data and the first-order kinetic rate plot for the polymerisations of BzMA by ATP are given in Figures 5.8 and 5.9 respectively.

Figure 5.8 Plot of Mn versus % monomer conversion for the ATP of BzMA in toluene at 90 °C

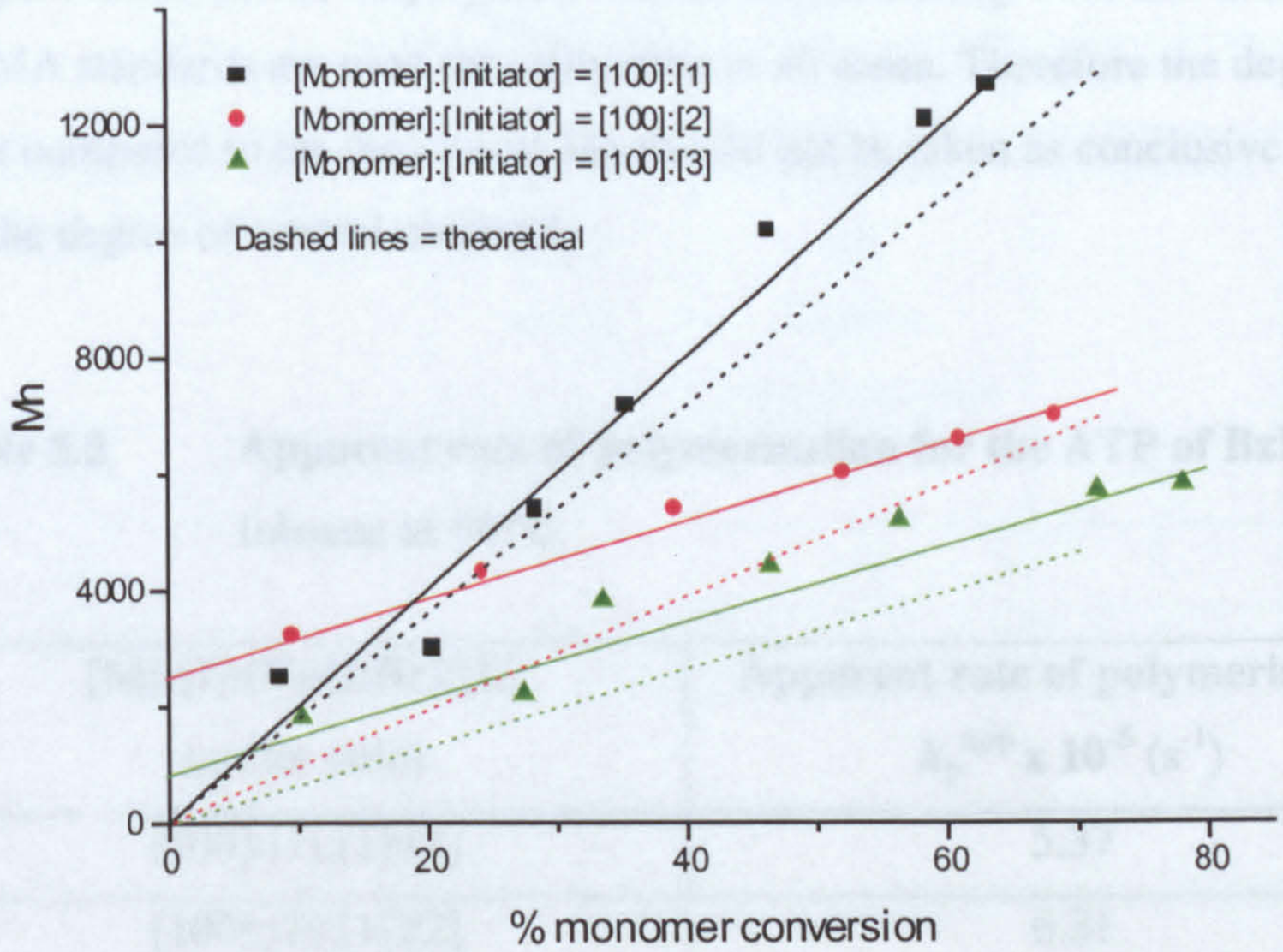
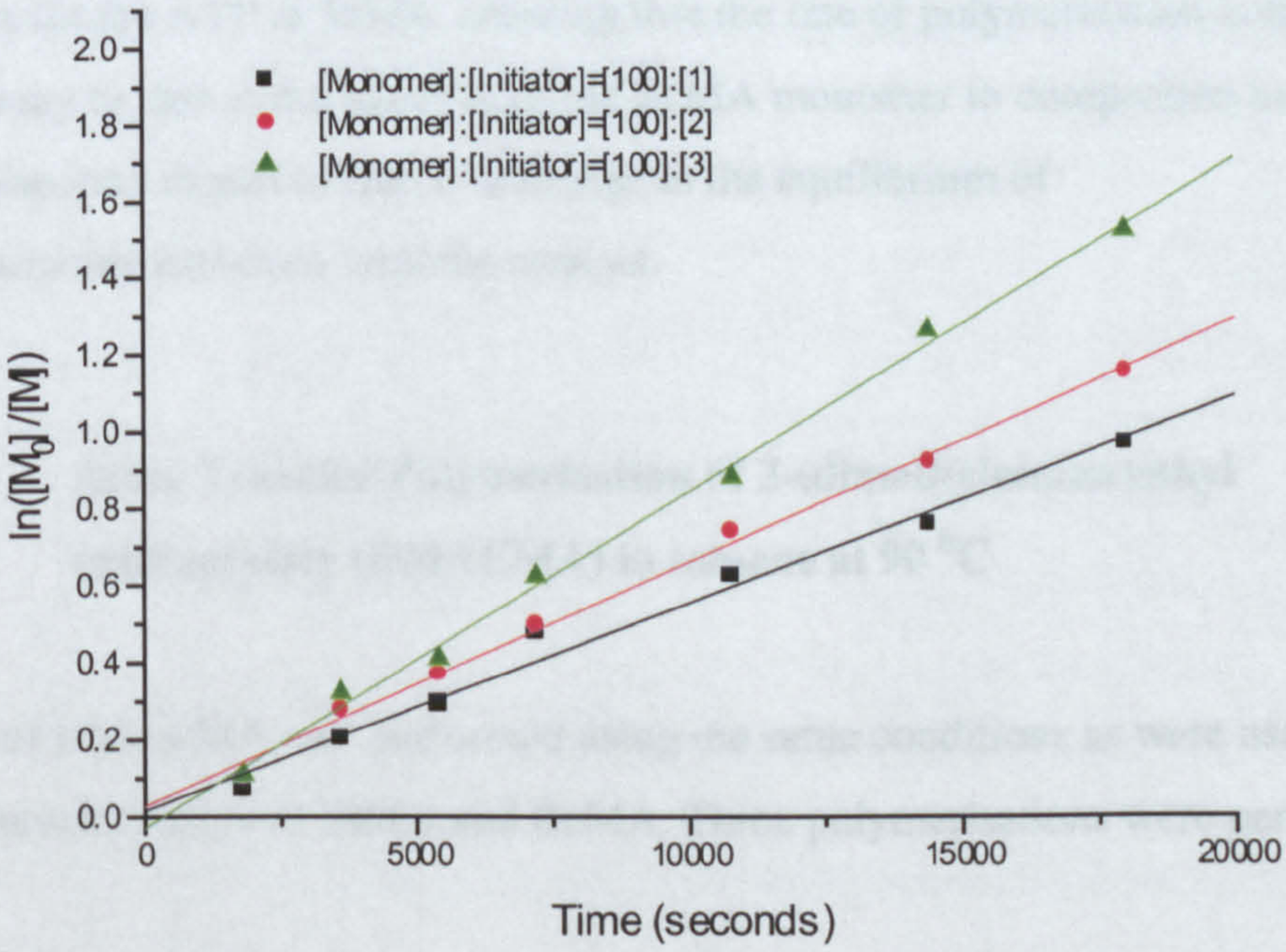


Figure 5.9 First-order kinetic rate plot for the ATP of BzMA in toluene at 90 °C



The data for ATP of BzMA show that controlled polymerisation is achieved. All polymers formed had a PDi < 1.4. Mn increases approximately linearly with % monomer conversion and the first-order rate plots are linear, indicating that the number of active species remains constant throughout the polymerisation and that the rate of termination is minimal. It should be noted that the molecular weight distribution of all polymers was determined using GPC and that narrow PMMA standards are used for calibration in all cases. Therefore the degree of error compared to the theoretical Mn should not be taken as conclusive evidence for the degree of control obtained.

Table 5.5 Apparent rate of polymerisation for the ATP of BzMA in toluene at 90 °C

[M]:[I]:[Cu(I)Br]:[L] (molar ratio)	Apparent rate of polymerisation k_p^{app} x 10^{-5} (s^{-1})
[100]:[1]:[1]:[2]	5.37
[100]:[2]:[1]:[2]	6.31
[100]:[3]:[1]:[2]	8.69

As expected, the apparent rate of reaction (k_p^{app}) increases as the initiator concentration is increased. The values for k_p^{app} are lower than the corresponding values for the ATP of MMA, showing that the rate of polymerisation is reduced. This may be due to the lower k_p of the BzMA monomer in comparison to MMA and also may in part be due to a change in the equilibrium of activation/deactivation with the catalyst.

5.1.4 Atom Transfer Polymerisation of 2-(dimethylamino)ethyl methacrylate (DMAEMA) in toluene at 90 °C

ATP of DMAEMA was performed using the same conditions as were used for the polymerisation of MMA and BzMA. Three polymerisations were performed

with different [Monomer]:[Initiator] ratios. Table 5.6 outlines the reagent composition for each reaction performed.

Table 5.6 Reaction conditions for the Atom Transfer Polymerisation of DMAEMA in toluene at 90 °C

		Molar ratio			
DMAEMA (g)	**Toluene** (g)	**Monomer [M]** BzMA	**Initiator [I]** Ethyl-2-bromoisobutyrate	**[Cu(I)Br]**	**Ligand [L]** n-pentyl
20	40	100	1	1	2
20	40	100	2	1	2
20	40	100	4	1	2

Table 5.7 lists the molecular weight and conversion data obtained by gravimetry from the extracts of the reaction where [Monomer]:[Initiator] = [100]:[2].

Table 5.7 Molecular weight and conversion data for ATP of DMAEMA with [Monomer]:[Initiator] = [100]:[2] in toluene at 90 °C

Sample (hours)	Mn	PDi	Conversion (%)	Theoretical Mn*
0.5	-	-	13.9	1300
1	-	-	29.9	2600
1.5	3200	1.71	44.3	3700
2	4200	2.27	55.9	4600
3	4800	2.30	72.8	5900
4	7000	1.74	81.0	6500
5	7400	1.88	86.8	6800

* The theoretical Mn values are calculated using equation 1.8 from chapter 1, section 1.5.2.

The molecular weight data for the polymerisations of DMAEMA by ATP are given in Figure 5.10.

Figure 5.10 Plot of Mn versus % monomer conversion for the ATP of DMAEMA in toluene at 90 °C

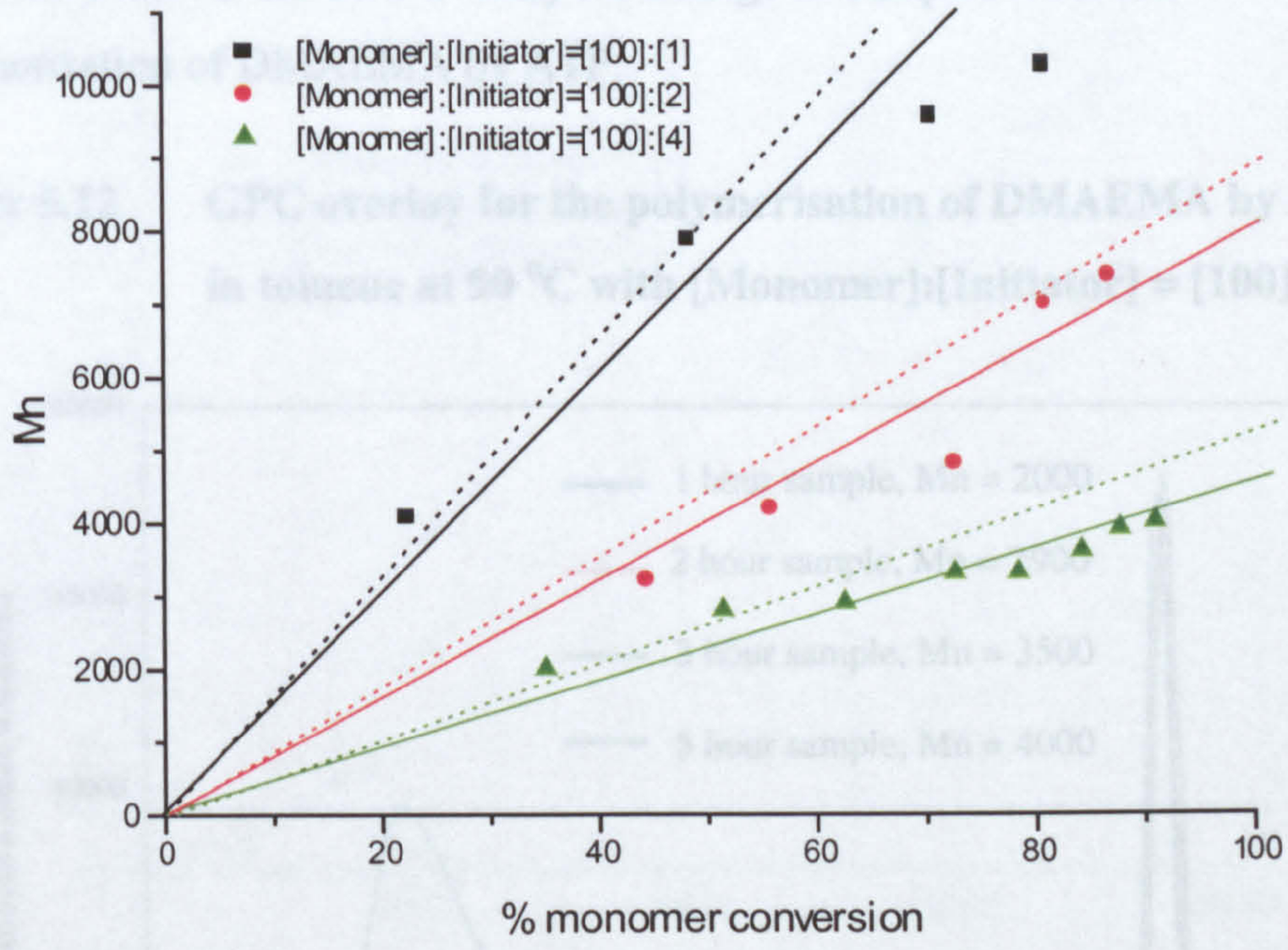


Figure 5.11 Plot of Polydispersity Index (PDi) versus time for the ATP of DMAEMA in toluene at 90 °C

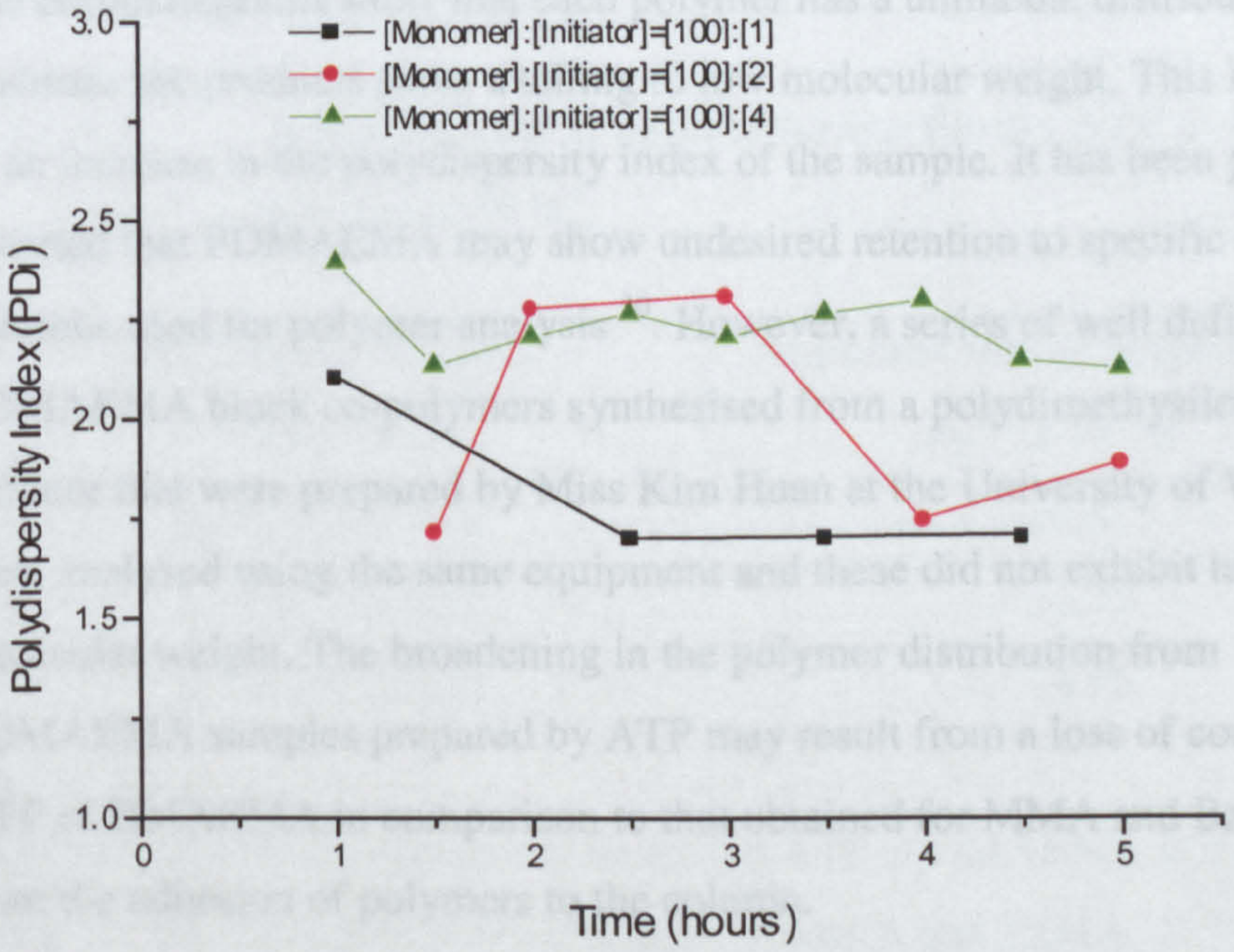
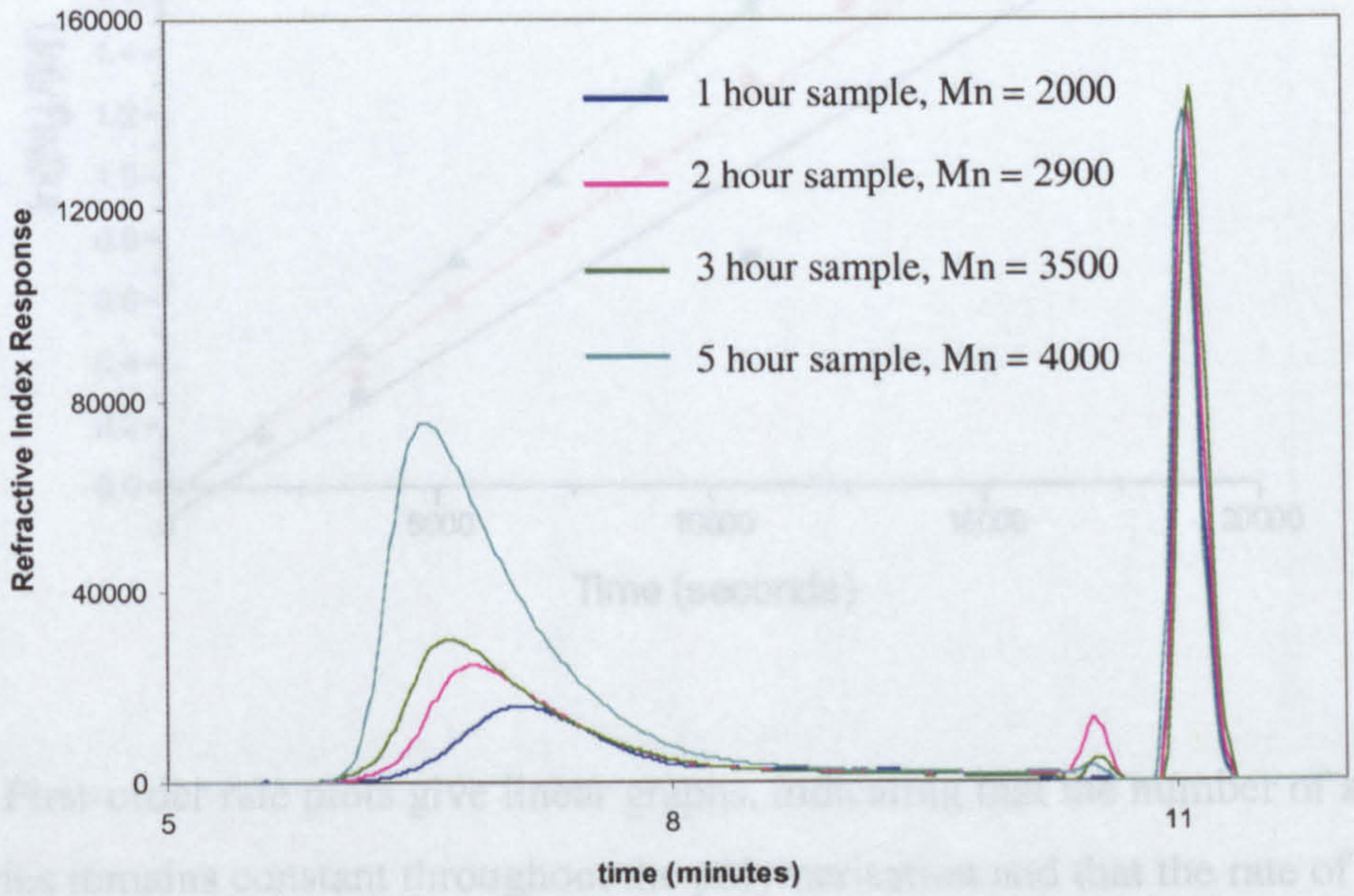


Figure 5.11 shows that as the relative concentration of initiator is increased with respect to monomer, an increase in the polydispersity index occurs. Typically the polymerisation of PDMAEMA gave a polydispersity index of 1.6 < PDi < 2.5.

Figure 5.12 shows the GPC overlay for a range of samples from the polymerisation of DMAEMA by ATP.

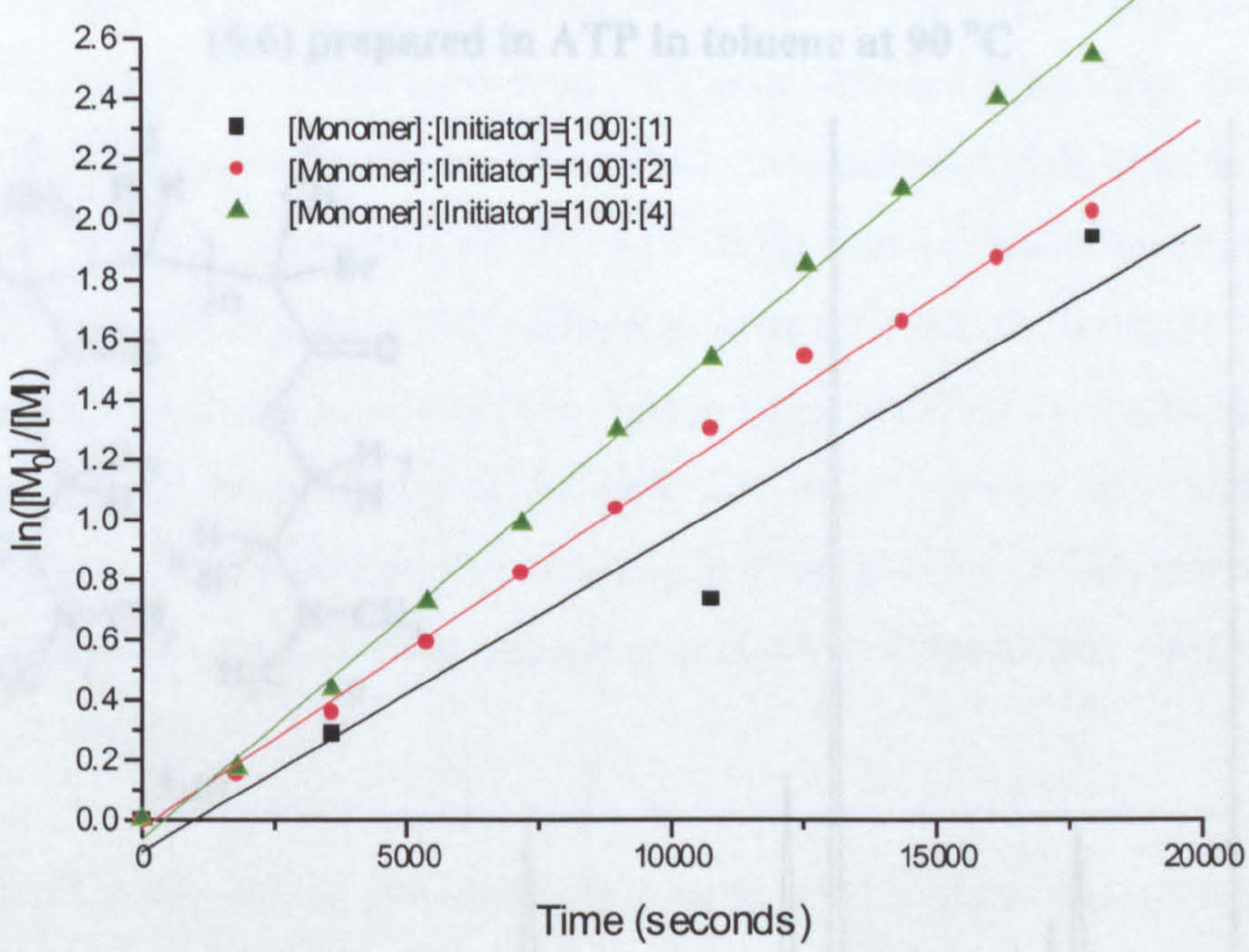
Figure 5.12 GPC overlay for the polymerisation of DMAEMA by ATP in toluene at 90 °C with [Monomer]:[Initiator] = [100]:[4]



The chromatograms show that each polymer has a unimodal distribution. For all reactions the products show a tailing to low molecular weight. This is observed as an increase in the polydispersity index of the sample. It has been previously reported that PDMAEMA may show undesired retention to specific GPC columns used for polymer analysis [30]. However, a series of well defined PDMAEMA block co-polymers synthesised from a polydimethysiloxane initiator that were prepared by Miss Kim Huan at the University of Warwick were analysed using the same equipment and these did not exhibit tailing to low molecular weight. The broadening in the polymer distribution from PDMAEMA samples prepared by ATP may result from a loss of control for the ATP of DMAEMA in comparison to that obtained for MMA and BzMA or from the adhesion of polymers to the column.

The First-order rate plot for the ATP of DMAEMA in toluene at 90 °C is given in Figure 5.13.

Figure 5.13 First-order kinetic rate plot for the ATP of DMAEMA in toluene at 90 °C



The First-order rate plots give linear graphs, indicating that the number of active species remains constant throughout the polymerisation and that the rate of termination is minimal.

Table 5.8 Apparent rate of polymerisation for the ATP of BzMA in toluene at 90 °C

[M]:[I]:[Cu(I)Br]:[L] (molar ratio)	**Apparent rate of polymerisation** k_p^{app} **x** 10^{-5} (s^{-1})
[100]:[1]:[1]:[2]	10.43
[100]:[2]:[1]:[2]	11.78
[100]:[4]:[1]:[2]	14.92

The apparent rate of polymerisation for the ATP of DMAEMA is higher than is found for corresponding polymerisations of MMA and BzMA.

The polymer products were purified by passing through a column of activated basic alumina and then oven dried to remove excess monomer. The ^1H NMR in $CDCl_3$ of the purified sample obtained from the ATP of DMAEMA [Monomer]:[Initiator] = [100]:[2] after 1.5 hours is given in Figure 5.14.

Figure 5.14 250 MHz, ^1H NMR in $CDCl_3$ of PDMAEMA homopolymer (5.6) prepared in ATP in toluene at 90 °C

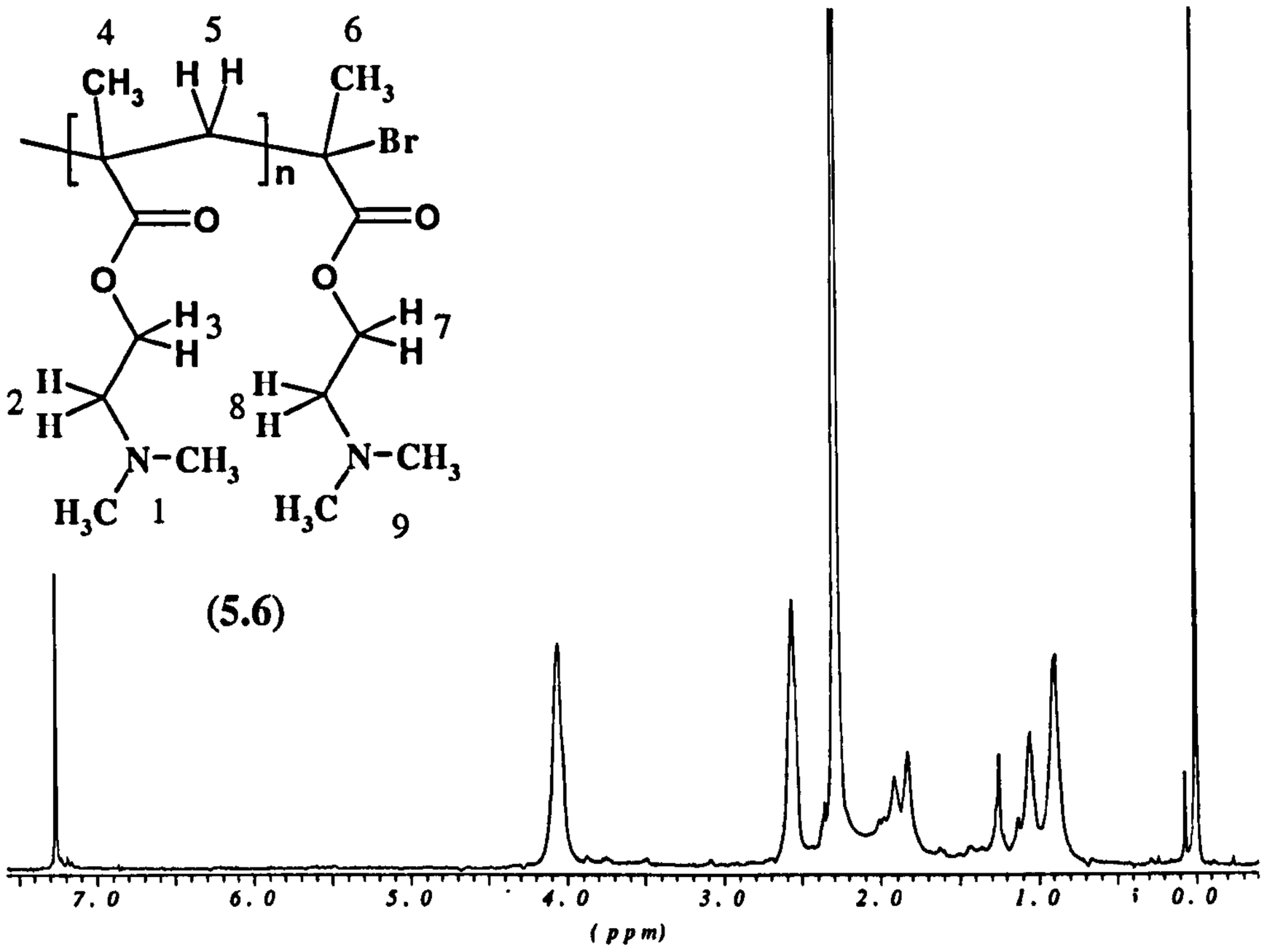


Table 5.9 Peak assignment for the 250 MHz, ^1H NMR in $CDCl_3$ of PDMAEMA (5.6) from ATP in toluene at 90 °C

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
7.27	Singlet	-	Solvent, $CDCl_3$
4.05	Singlet	1.08	H^2, H^8
2.56	Multiplet	1.04	H^3, H^7
2.28	Singlet	3.29	H^1, H^9
1.91	Multiplet	0.91	H^5
1.06	Multiplet	2.39	H^4, H^6
0	Singlet	-	TMS

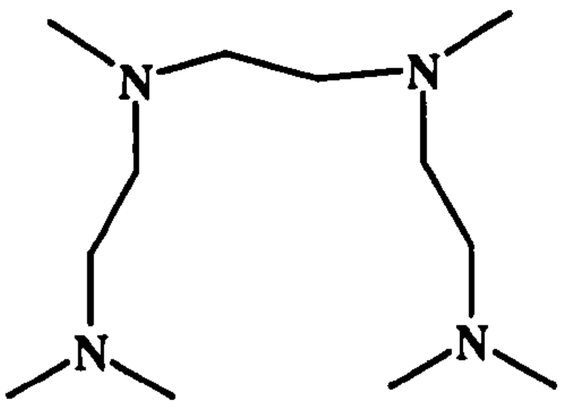
Haddleton *et al* have previously shown that the ^{1}H NMR analysis of low molecular weight PMMA can be used to identify the methoxy functionality α to the terminal bromine [16,31]. The proton signal for the methoxy functionality α to the terminal bromine in PMMA is located at 3.82 ppm in deuterated chloroform. End group analysis of the α methoxy peak in comparison to the backbone chain was shown to be useful for calculating the molecular mass of the polymer, with the data showing excellent agreement with those obtained from GPC. The 250 MHz ^{1}H NMR spectrum of the PDMAEMA homopolymer (**5.6**) from the reaction where [Monomer]:[Initiator] = [100]:[2] after 1.5 hours does not exhibit a defined signal for the O-CH_2-R protons (H^7) α to the bromine. The molecular weight of the polymer may be too large, resulting in a reduction of the intensity of end group signal and the O-CH_2-R (H^3) groups may exhibit a large degree of peak broadening, resulting in overlap of the O-CH_2-R protons (H^7) α to the bromine. Further end group analysis of PDMAEMA homopolymer is given in section 5.1.9.

The data for the ATP of DMAEMA in toluene at 90 °C show that molecular weight increases linearly with respect to % monomer conversion and that the apparent rate of polymerisation is first-order with respect to the active species. All polymers showed a tailing to low molecular weight and this is interpreted as a loss of control during polymerisation. The ^{1}H NMR analysis of the PDMAEMA homopolymer from ATP does not provide confirmation that the ω-terminal bromine functionality is included.

5.1.5 Atom Transfer Polymerisation of 2-(dimethylamino)ethyl methacrylate (DMAEMA) in different solvent systems

Matyjaszewski has previously shown that, for the ATP of DMAEMA using Cu(I)Br with 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (**5.7**) ligands, as the solvent polarity is increased, the degree of control is improved [32]. Matyjaszewski showed that ATP of DMAEMA in dichlorobenzene produced narrow polydispersity polymers with PDi is < 1.5 [25,32].

Figure 5.15 Atom Transfer Polymerisation Ligand, 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (5.7)



(HMTETA) (5.7)

Polymerisation of DMAEMA monomer by ATP using Cu(I)Br with N-(pentyl)-2-pyridylmethanimine ligands was performed with several different solvents. This allowed for a comparison to be made to determine the effect of solvent on the degree of control obtained. Polymerisation was performed in bulk, in methanol and in dichlorobenzene solution. Each reaction was performed with [Monomer]:[Initiator]:[Cu(I)Br]:[Ligand] = [100]:[2]:[1]:[2] and/or [100]:[1]:[1]:[2].

Table 5.10 Reaction conditions for the Atom Transfer Polymerisation of DMAEMA in different solvents

Solvent	[M]:[I]:[Cu(I)Br]:[L]	Reaction Temperature (°C)
None (Bulk)	[100]:[2]:[1]:[2]	60
Methanol	[100]:[1]:[1]:[2] [100]:[2]:[1]:[2]	40
Dichlorobenzene	[100]:[1]:[1]:[2]	90
H_2O	[100]:[1]:[1]:[2] [100]:[2]:[1]:[2]	90

No polymer was obtained from the solution polymerisations performed in water. This is now known to be the result of the hydrolytic decomposition of

DMAEMA in water to produce methacrylic acid [33]. The molecular weight data and polydispersity index from all other reactions are plotted against time.

Figure 5.16 Plot of Mn versus % monomer conversion for the ATP of DMAEMA in different solvent systems

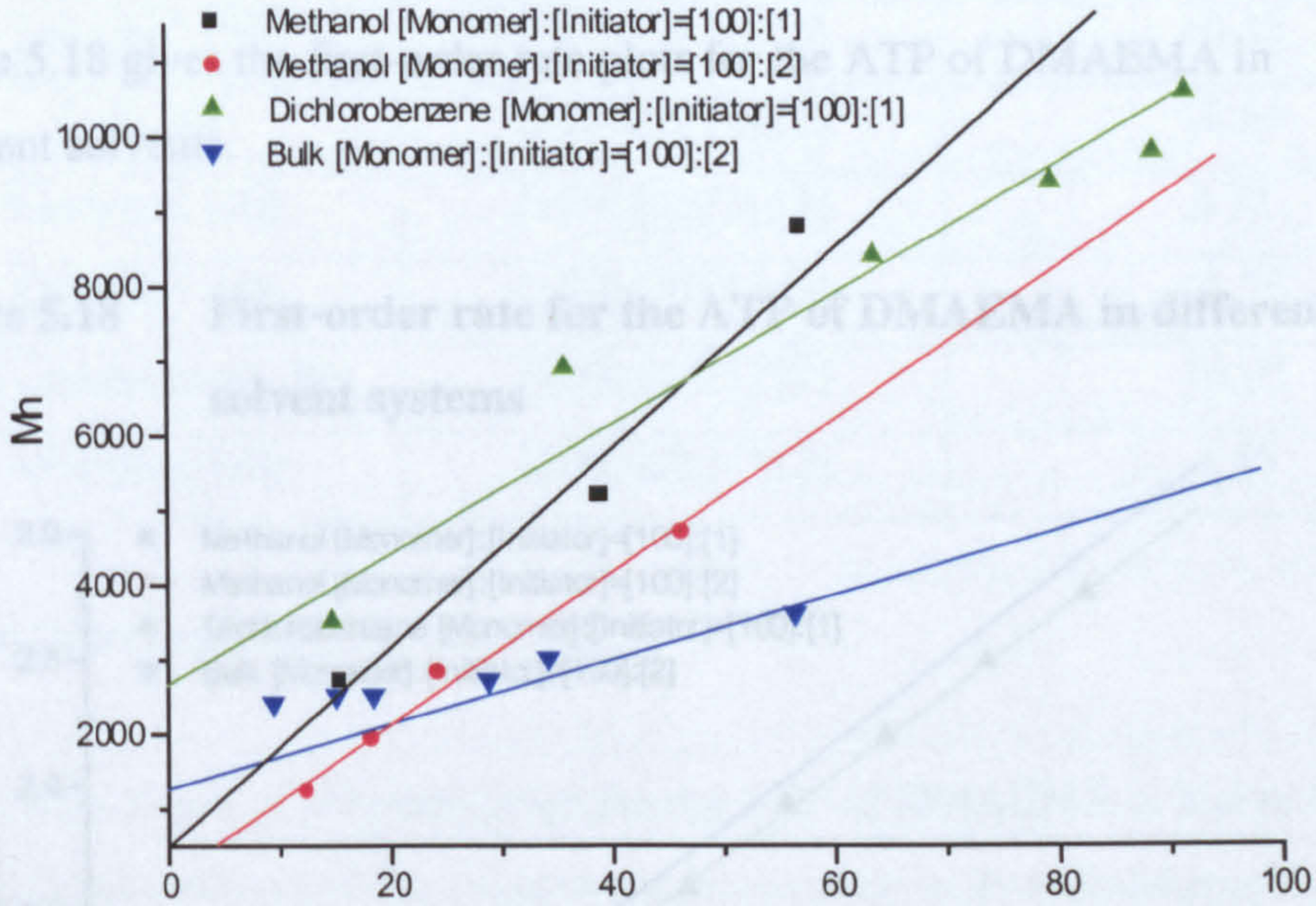
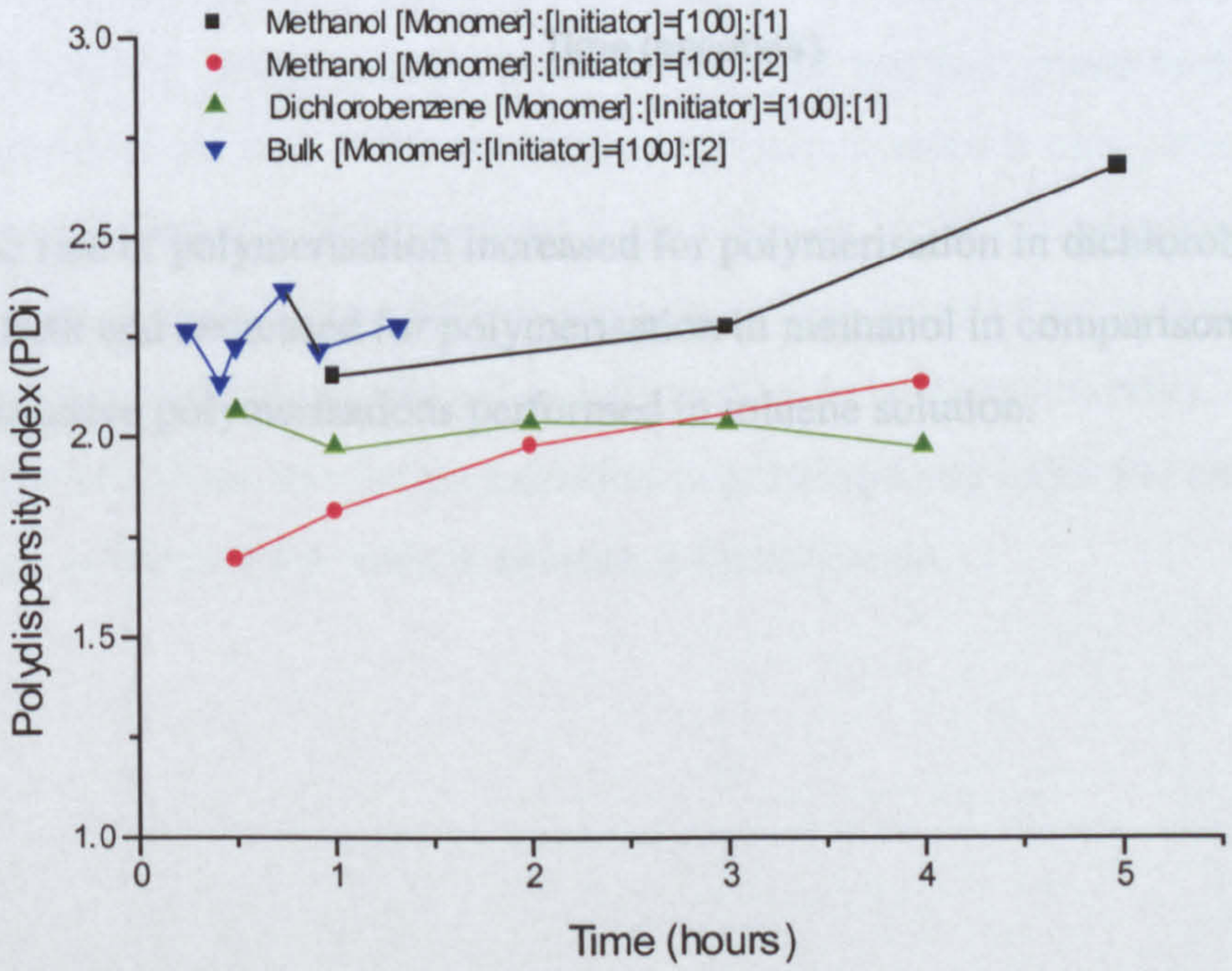


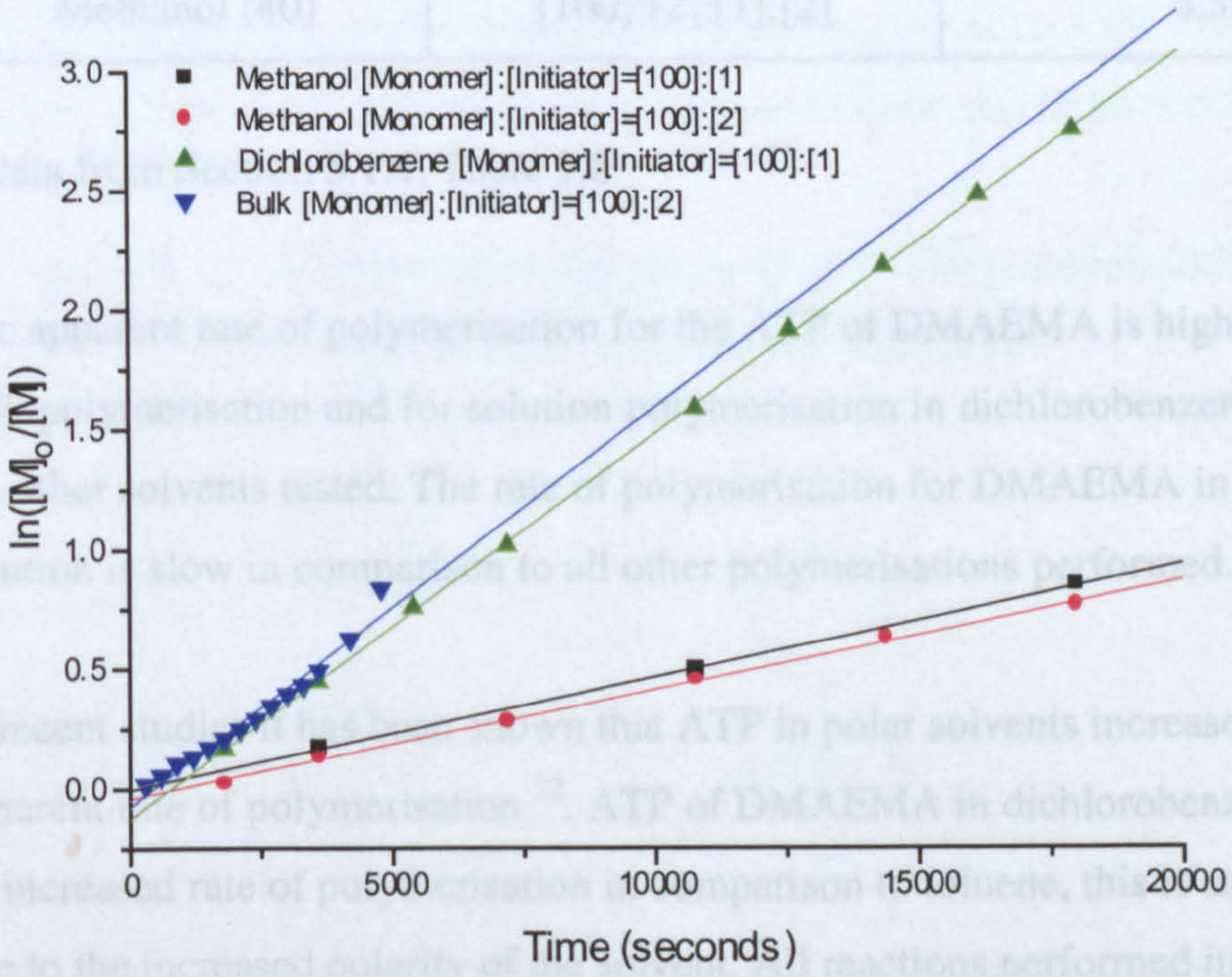
Figure 5.17 Plot of Polydispersity Index (PDi) versus time for the ATP of DMAEMA in different solvent systems



The plot of molecular weight versus % monomer conversion shows that all polymerisations proceed with a linear molecular weight increase. The plot of polydispersity index versus time shows that no significant reduction in the polydispersity index of the product is achieved by using a more polar solvent or by using bulk polymerisation in comparison to toluene.

Figure 5.18 gives the first-order rate plots for the ATP of DMAEMA in different solvents.

Figure 5.18 First-order rate for the ATP of DMAEMA in different solvent systems



The rate of polymerisation increased for polymerisation in dichlorobenzene and in bulk and decreased for polymerisation in methanol in comparison to the respective polymerisations performed in toluene solution.

Table 5.11 Apparent rate of polymerisation for the ATP of DMAEMA in different solvent systems

Solvent (Temp, °C)	[M]:[I]:[Cu(I)Br]:[L] (molar ratio)	Apparent rate of polymerisation k_p^{app} x 10^{-5} (s^{-1})
Toluene* (90)	[100]:[1]:[1]:[2]	10.43
Bulk (60)	[100]:[1]:[1]:[2]	16.64
Methanol (40)	[100]:[1]:[1]:[2]	4.71
Toluene* (90)	[100]:[2]:[1]:[2]	11.78
Dichlorobenzene (90)	[100]:[2]:[1]:[2]	16.05
Methanol (40)	[100]:[2]:[1]:[2]	4.55

* Data from Section 5.1.4, Table 5.8

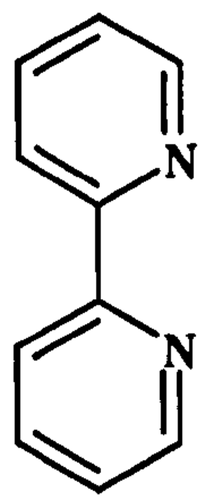
The apparent rate of polymerisation for the ATP of DMAEMA is higher for bulk polymerisation and for solution polymerisation in dichlorobenzene than for the other solvents tested. The rate of polymerisation for DMAEMA in methanol solution is slow in comparison to all other polymerisations performed.

In recent studies it has been shown that ATP in polar solvents increases the apparent rate of polymerisation [32]. ATP of DMAEMA in dichlorobenzene gave an increased rate of polymerisation in comparison to toluene, this is as expected due to the increased polarity of the solvent. All reactions performed in methanol showed a reduction in the rate of polymerisation which is unexpected due to the increased polarity of this solvent. This reduction in the rate of polymerisation may however be due to the reduction in reaction temperature in comparison to the other reactions performed and differences in catalyst solubility. All polymerisations showed no reduction in polydispersity index in comparison to those products from toluene solution polymerisation.

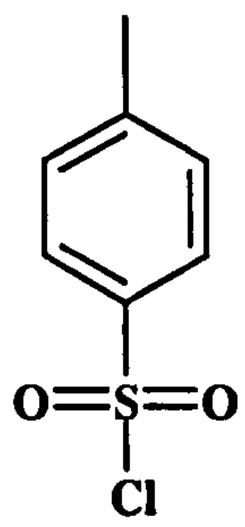
5.1.6 Atom Transfer Polymerisation of 2-(dimethylamino)ethyl methacrylate (DMAEMA) with different initiator and ligand systems

Atom transfer polymerisation of DMAEMA monomer was performed with a different initiator and with a different ligand system to determine how the use of other known reagents for ATP would alter the degree of control obtained. Both polymerisations were performed with analogous conditions to those used for the polymerisation of DMAEMA in toluene solution, as outlined in section 5.1.4. Polymerisation was performed using the 2,2'-bipyridine (bpy) ligand systems as pioneered by Matyjaszewski and co-workers [2,8]. Another polymerisation was performed using *p*-toluenesulfonyl chloride as an alternative ATP initiator. Table 5.12 lists the experimental conditions for all polymerisations performed.

Figure 5.19 2,2'-bipyridine (bpy) ligand (5.8) and *p*-toluenesulfonyl chloride initiator (5.9) for use with ATP



2,2'-bipyridine (bpy) (**5.8**)



p-toluenesulfonyl chloride (**5.9**)

Table 5.12 Reaction conditions for the Atom Transfer Polymerisation of DMAEMA in toluene at 90° C with different initiator and ligand systems

Monomer [M]	Initiator [I]	Initiator Type	[Cu(I)Br]	Ligand [L]	Ligand Type
100	2	Ethyl-2-bromoisobutyrate (**5.3**)	1	2	Bpy (**5.8**)
100	1	*p*-toluenesulfonyl chloride (**5.9**)	1	2	n-pentyl (**5.2**)

A degree of controlled polymerisation was obtained for the polymerisation containing bpy as a ligand. No controlled polymerisation was obtained where polymerisation was initiated with p-toluenesulfonyl chloride. The monomer conversion after 24 hours was 24 % with a polymer of Mn = 24000 compared with a theoretical Mn of 3800. Figure 5.20 shows the plot for molecular weight versus time for reaction containing bpy as a ligand in comparison with the data for analogous polymerisation with N-(n-pentyl)-2-pyridylmethanimine as a ligand (data taken from Section 5.1.4).

Figure 5.20 Plot of Mn versus % monomer conversion for the ATP of DMAEMA in toluene at 90 °C with a change of ligand

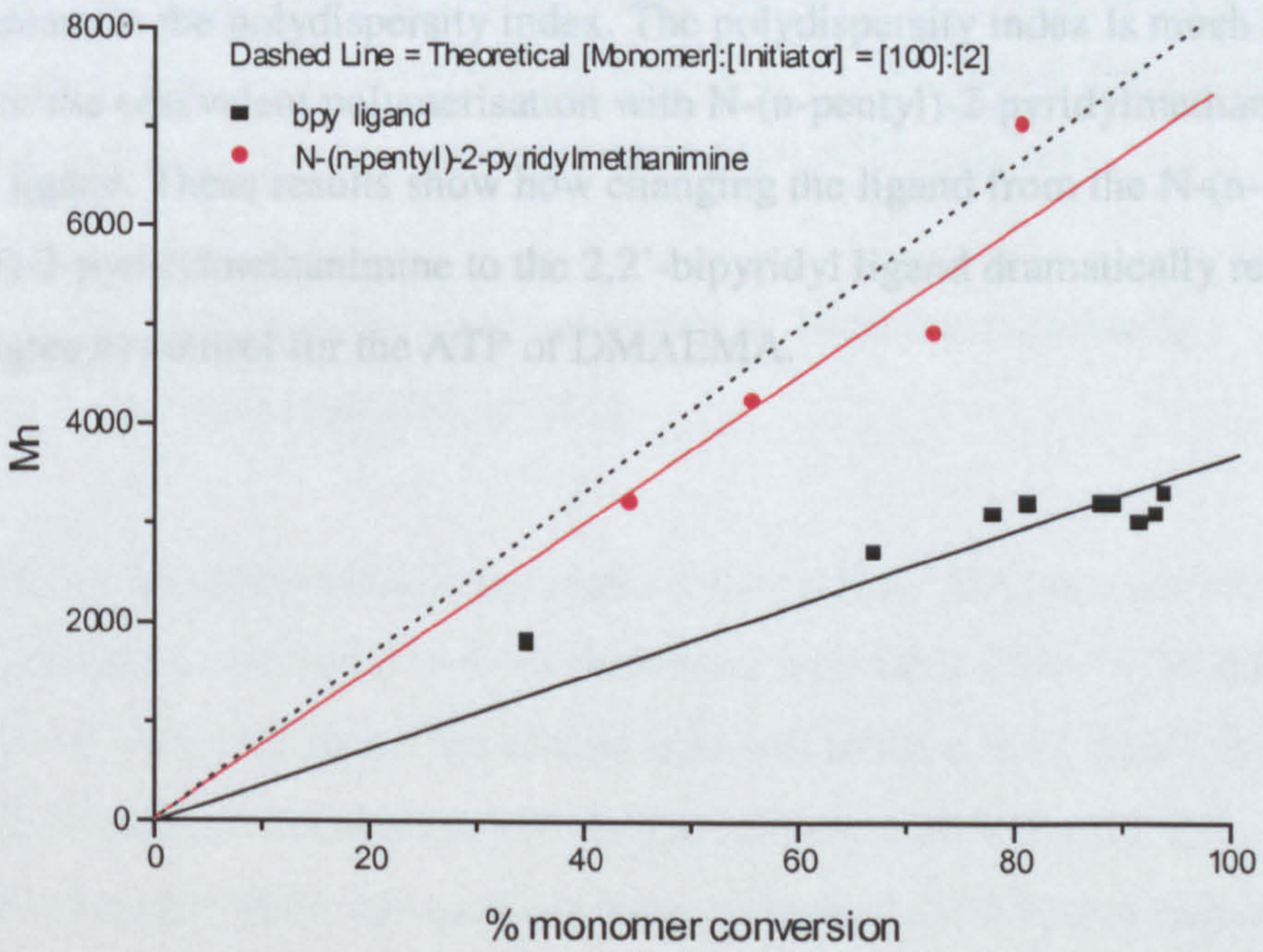


Figure 5.21 Plot of Polydispersity Index versus time for the ATP of DMAEMA in toluene at 90 °C with a change of ligand

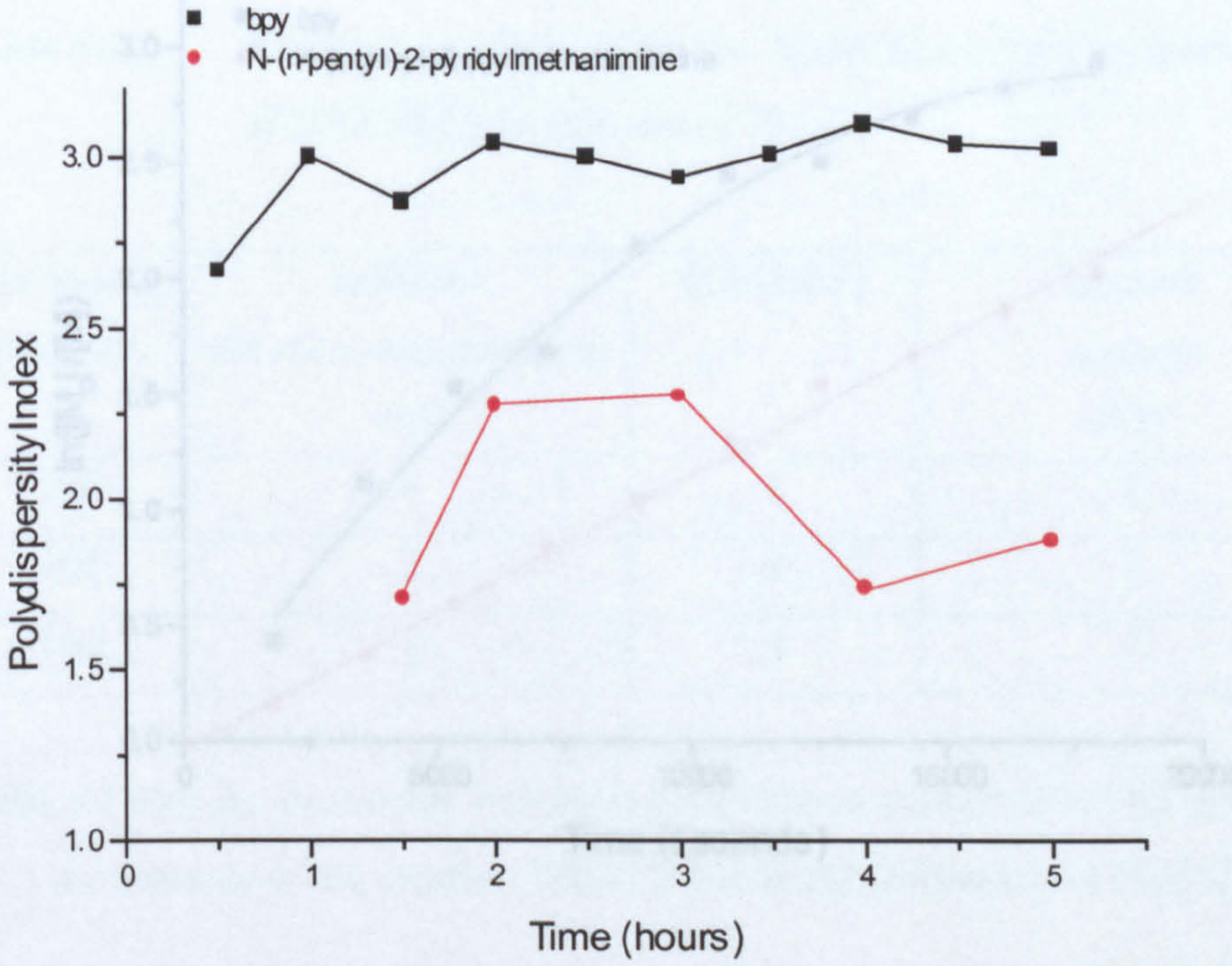
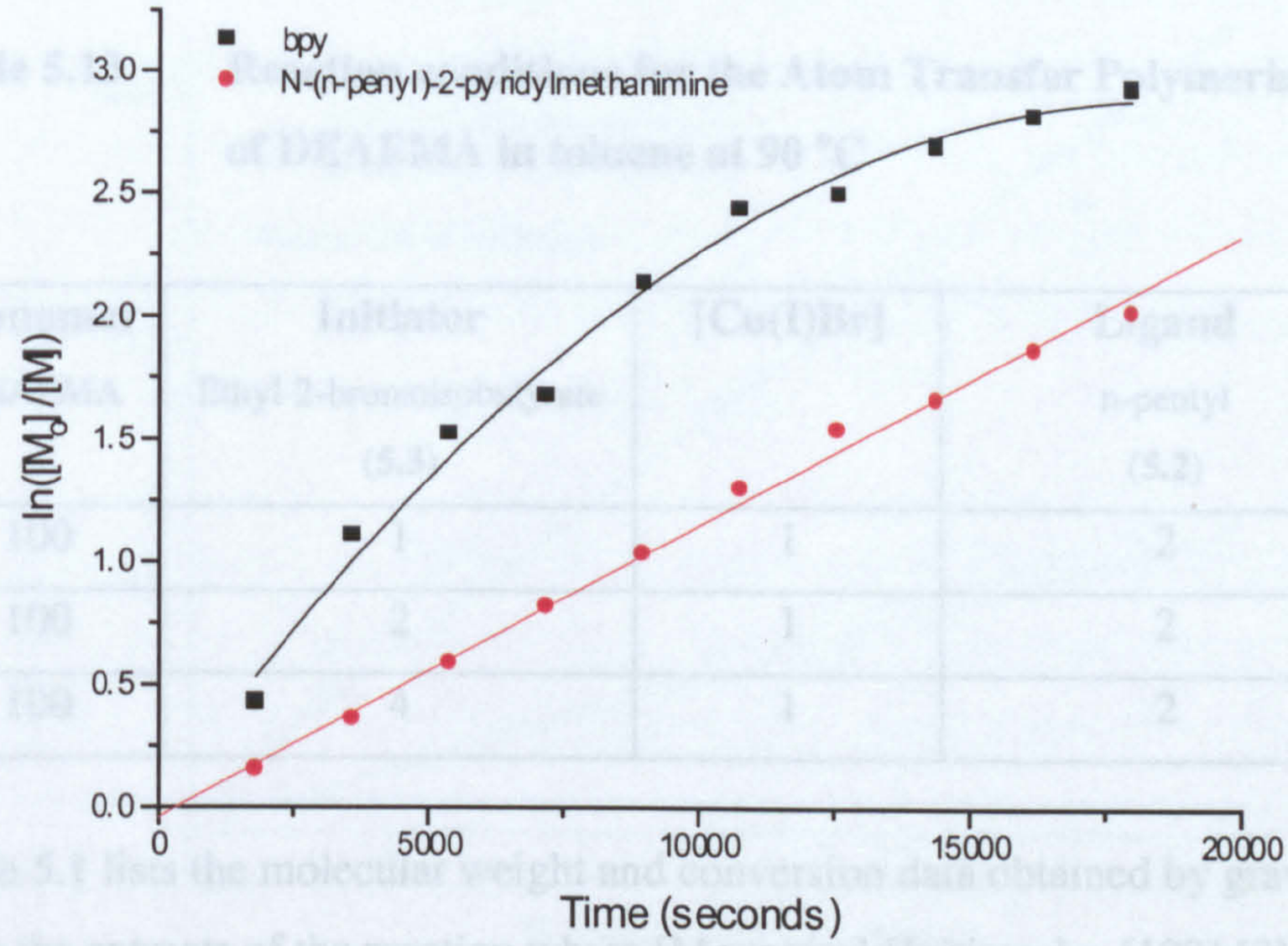


Figure 5.20 shows that molecular weight increases approximately linearly with respect to % monomer conversion. The reaction containing bpy as ligand shows that the molecular weight at 96 % monomer conversion is Mn = 3300; this is much lower than the predicted Mn = 8100. The reduction in Mn compared to theory is shown by GPC to be the result of tailing to low molecular weight. A number of low molecular weight species lead to an overall reduction in Mn and an increase in the polydispersity index. The polydispersity index is much higher than for the equivalent polymerisation with N-(n-pentyl)-2-pyridylmethanimine as the ligand. These results show how changing the ligand from the N-(n-pentyl)-2-pyridylmethanimine to the 2,2'-bipyridyl ligand dramatically reduces the degree of control for the ATP of DMAEMA.

Figure 5.22 First-order rate for the ATP of DMAEMA in toluene at 90 °C with a change of ligand



The first-order rate plot shows that when the polymerisation is performed with bpy ligand a linear kinetic rate plot is not obtained. This shows that a degree of termination occurs during polymerisation and that this results in a reduction in the concentration of active species present in the reaction. Depending on the type of termination that takes place, it would be expected that a degree of low molecular weight product would be produced. Monomer would continue to propagate with the remaining active species, resulting in a broadening of the polydispersity index and an overall reduction in the Mn. All of these features are observed in the analysis of the products from ATP with bpy.

5.1.7 Atom Transfer Polymerisation of 2-(diethylamino)ethyl methacrylate (DEAEMA)

The ATP of 2-(diethylamino)ethyl methacrylate (DEAEMA) was performed using analogous conditions to those performed with DMAEMA in Section 5.1.4. In all polymerisations the solvent used was toluene, the ligand was N-(n-pentyl)-2-pyridylmethanimine (**5.2**) and the initiator used was ethyl-2-bromoisobutyrate (**5.3**). All reactions were performed at 90 °C and each was

performed with 33% solids. The concentration was varied with respect to monomer. The reaction compositions are given in Table 5.13.

Table 5.13 Reaction conditions for the Atom Transfer Polymerisation of DEAEMA in toluene at 90 °C

Monomer DEAEMA	**Initiator** Ethyl-2-bromoisobutyrate **(5.3)**	**[Cu(I)Br]**	**Ligand** n-pentyl **(5.2)**
100	1	1	2
100	2	1	2
100	4	1	2

Table 5.1 lists the molecular weight and conversion data obtained by gravimetry from the extracts of the reaction where [Monomer]:[Initiator] = [100]:[2].

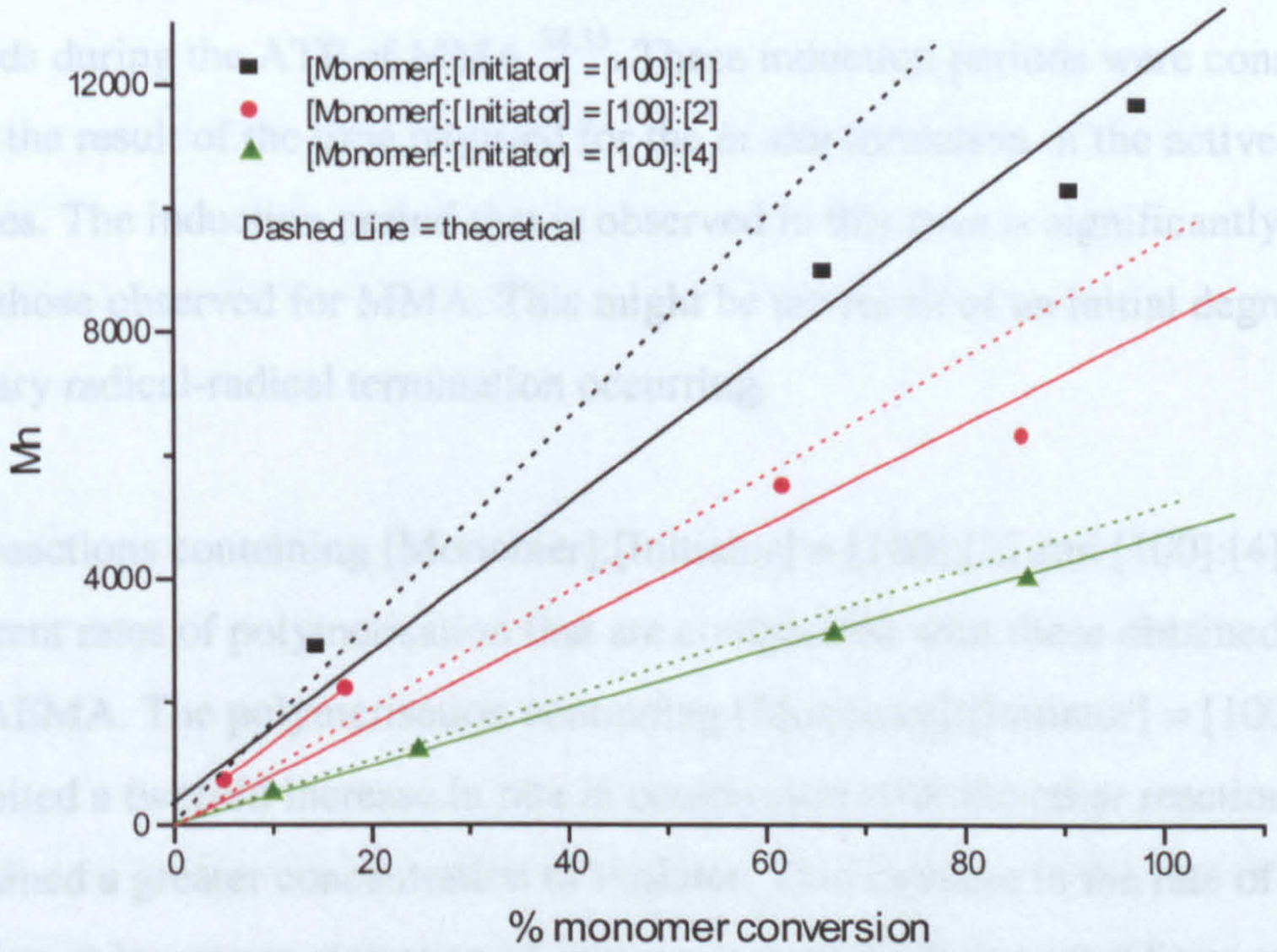
Table 5.14 Molecular weight and conversion data for ATP of DEAEMA with [Monomer]:[Initiator] = [100]:[2] in toluene at 90 °C

Sample (hours)	**Mn**	**PDi**	**Conversion** (%)	**Theoretical Mn***
2	700	1.25	5.2	670
3	2200	1.72	17.4	1800
4	5500	1.89	61.7	5900
5	6300	1.79	85.8	8100

* The theoretical Mn values are calculated using equation 1.8 from chapter 1 section 1.5.2.

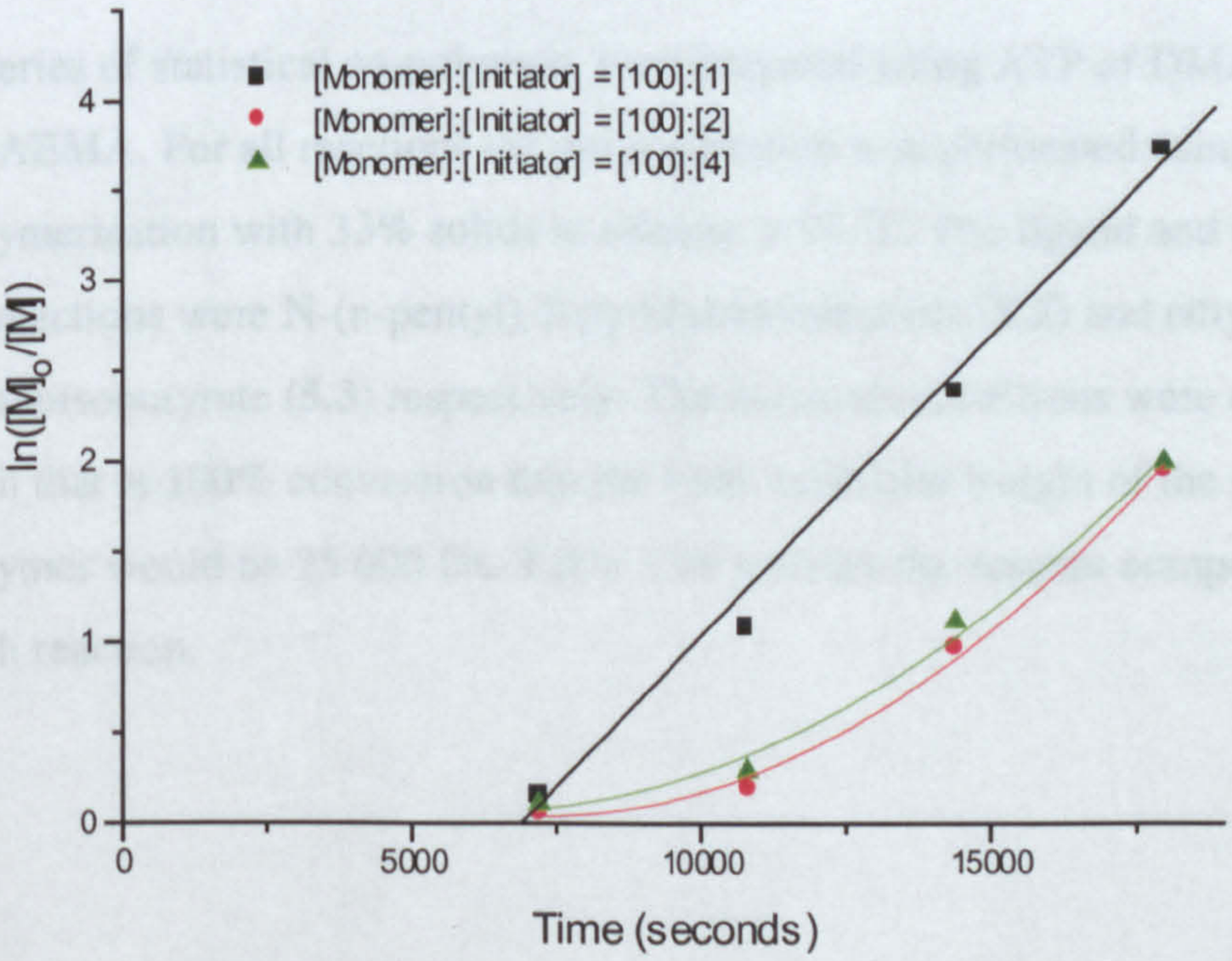
The molecular weight data for the reactions containing [Monomer]:[Initiator] = [100]:[1], [100]:[2] and [100]:[4] are plotted as molecular weight versus % monomer conversion.

Figure 5.23 Plot of Mn versus time for the ATP of DEAEMA in toluene at 90 °C



The obtained molecular weights of the product polymers agree well with the theoretical molecular weights.

Figure 5.24 First-order kinetic rate plot for the ATP of DEAEMA in toluene at 90 °C



The first-order rate plots show that the number of active species increases as the reaction takes place. For all reactions there is a long induction period before polymerisation begins. Haddleton *et al* observed the presence of induction periods during the ATP of MMA [34,35]. These induction periods were considered to be the result of the time required for the *in situ* formation of the active Cu(II) species. The induction period that is observed in this case is significantly longer than those observed for MMA. This might be the result of an initial degree of primary radical-radical termination occurring.

The reactions containing [Monomer]:[Initiator] = [100]:[2] and [100]:[4] show apparent rates of polymerisation that are comparable with those obtained from DMAEMA. The polymerisation containing [Monomer]:[Initiator] = [100]:[1] exhibited a twofold increase in rate in comparison with the other reactions that contained a greater concentration of initiator. This increase in the rate of reaction at lower concentration of initiator is potentially incurred from errors due to impurity or from conversion data.

5.1.8 Statistical co-polymerisation of 2-(diethylamino)ethyl methacrylate (DEAEMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) by ATP in toluene at 90 °C

A series of statistical co-polymers were prepared using ATP of DMAEMA and DEAEMA. For all reactions the polymerisation was performed using solution polymerisation with 33% solids in toluene at 90 °C. The ligand and initiator for all reactions were N-(n-pentyl)-2-pyridylmethanimine (**5.2**) and ethyl-2-bromoisobutyrate (**5.3**) respectively. The reactions conditions were determined such that at 100% conversion that the final molecular weight of the product polymer would be 25 000 Da. Table 5.16 outlines the reagent composition for each reaction.

Table 5.15 Reaction conditions for the Atom Transfer Co-Polymerisation of DMAEMA with DEAEMA in toluene at 90 °C

Monomer M^1 DMAEMA	**Monomer M^2** DEAEMA	**Total Monomer M^1+M^2**	**Initiator** Ethyl-2-bromoisobutyrate **(5.3)**	**Cu(I)Br**	**Ligand** n-pentyl **(5.2)**
114	38	152	1	1	2
73	73	146	1	1	2
35	105	140	1	1	2

Figure 5.22 shows the plot for molecular weight versus time for the reactions performed.

Figure 5.25 Plot of Mn versus time for the statistical co-polymerisation of DMAEMA and DEAEMA by ATP in toluene at 90 °C

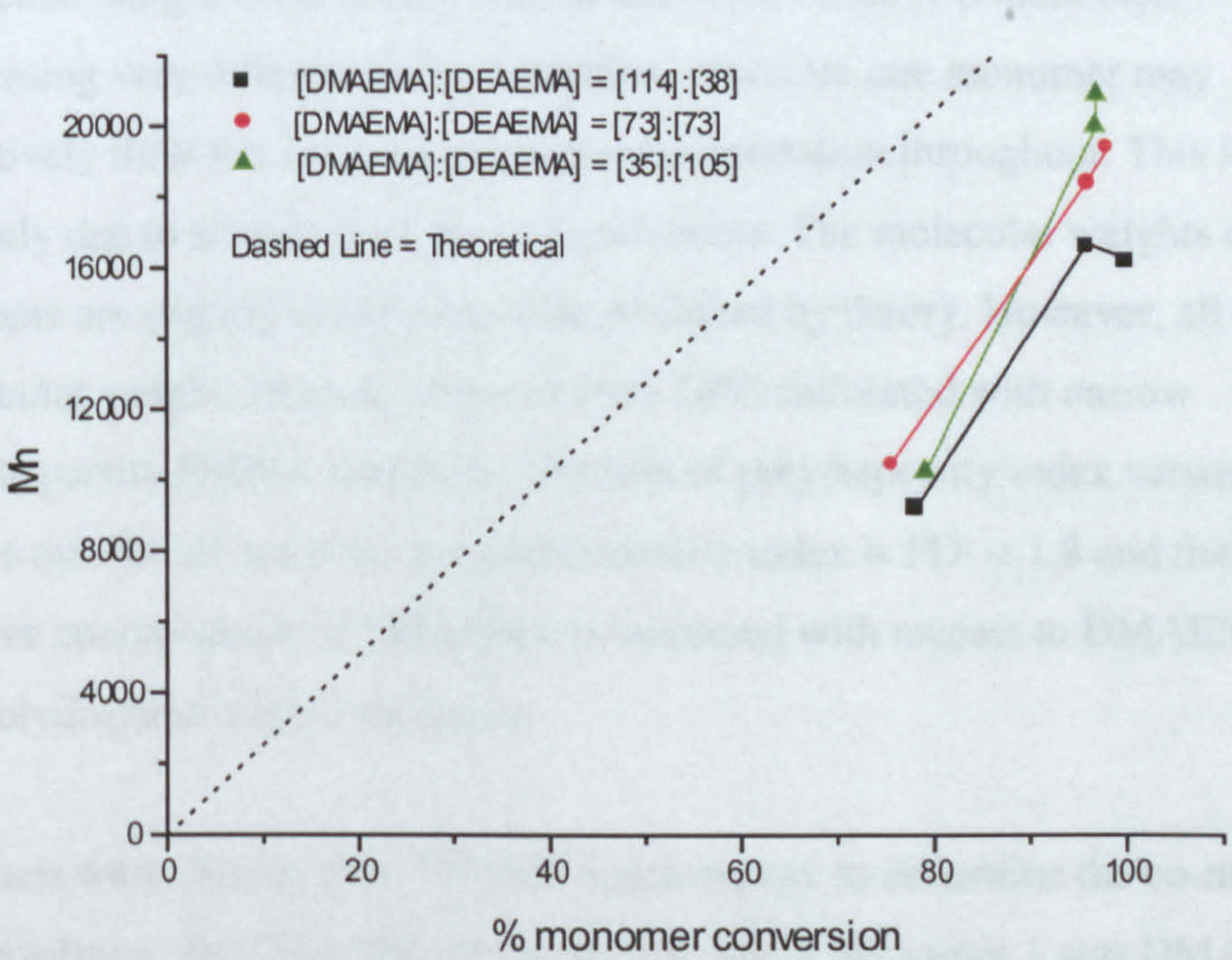
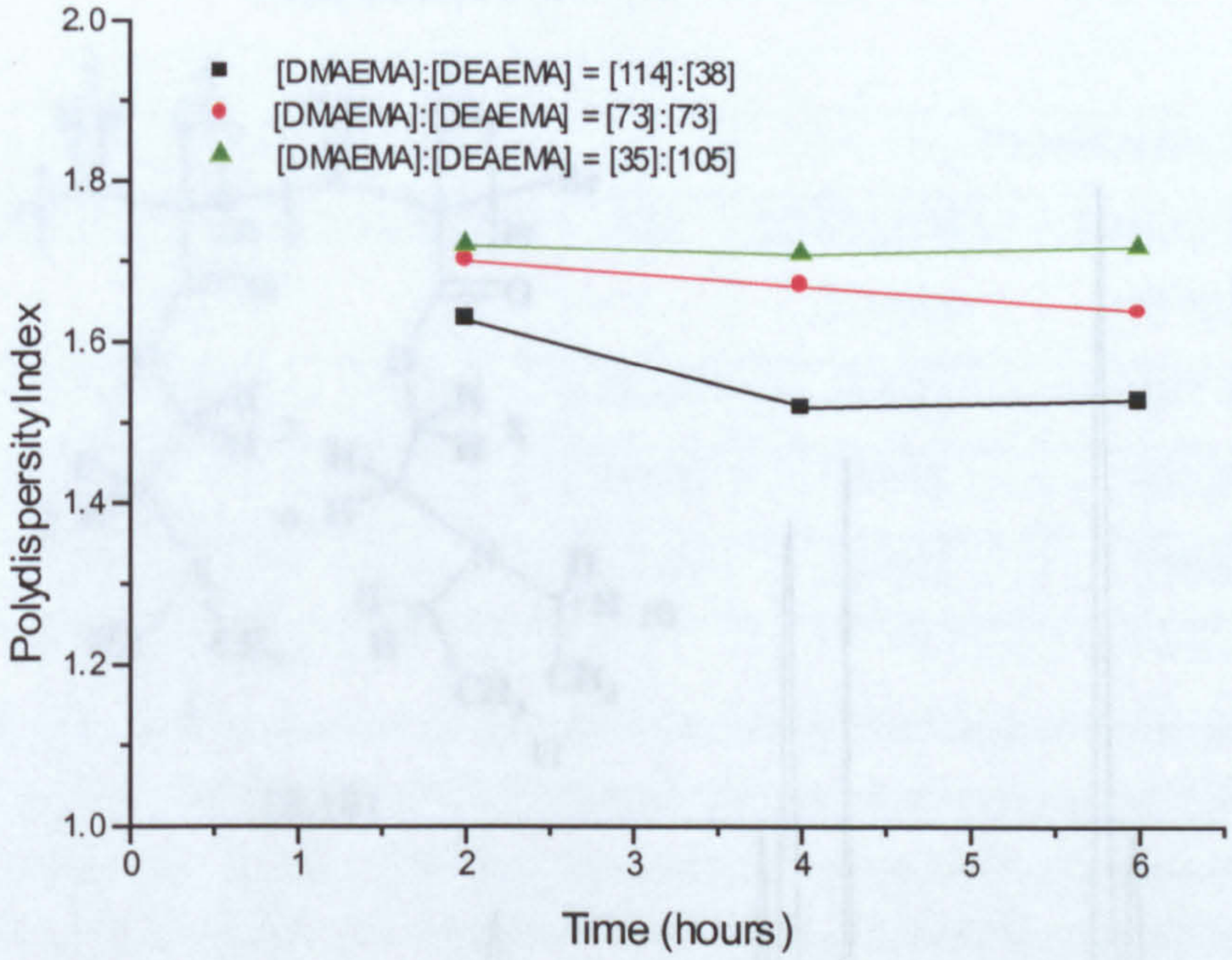


Figure 5.26 Plot of Polydispersity Index versus time for the statistical co-polymerisation of DMAEMA and DEAEMA by ATP in toluene at 90 °C



The plot of molecular weight versus % monomer conversion shows that the molecular weight increase below 50 % monomer conversion is very low and as the degree of monomer conversion approaches 100 % then rapid increase in molecular weight occurs. This may be the result of the two monomers possessing very different rates of reaction, therefore one monomer may effectively limit the available monomer concentration throughout. This is unlikely due to similarity of the two monomers. The molecular weights of the products are slightly lower than those predicted by theory. However, all of the molecular weight data was obtained from GPC calibrated with narrow polydispersity PMMA standards. The plot of polydispersity index versus time shows that for all reactions the polydispersity index is PDi < 1.8 and that as the relative concentration of DEAEMA is increased with respect to DMAEMA then the polydispersity index increases.

Products were analysed by ^{1}H NMR spectroscopy to determine the co-monomer compositions. The ^{1}H NMR for the sample where Monomer 1 was DMAEMA and where Monomer 2 was DEAEMA and the relative concentration of $[M^{1}]$:$[M^{2}]$ was [25]:[75] is given in figure 5.27.

Figure 5.27 **250 MHz, ^{1}H NMR in $CDCl_3$ of PDMAEMA-co-PDEAEMA [25]:[75] statistical co-polymer (5.10) prepared in ATP in toluene at 90 °C**

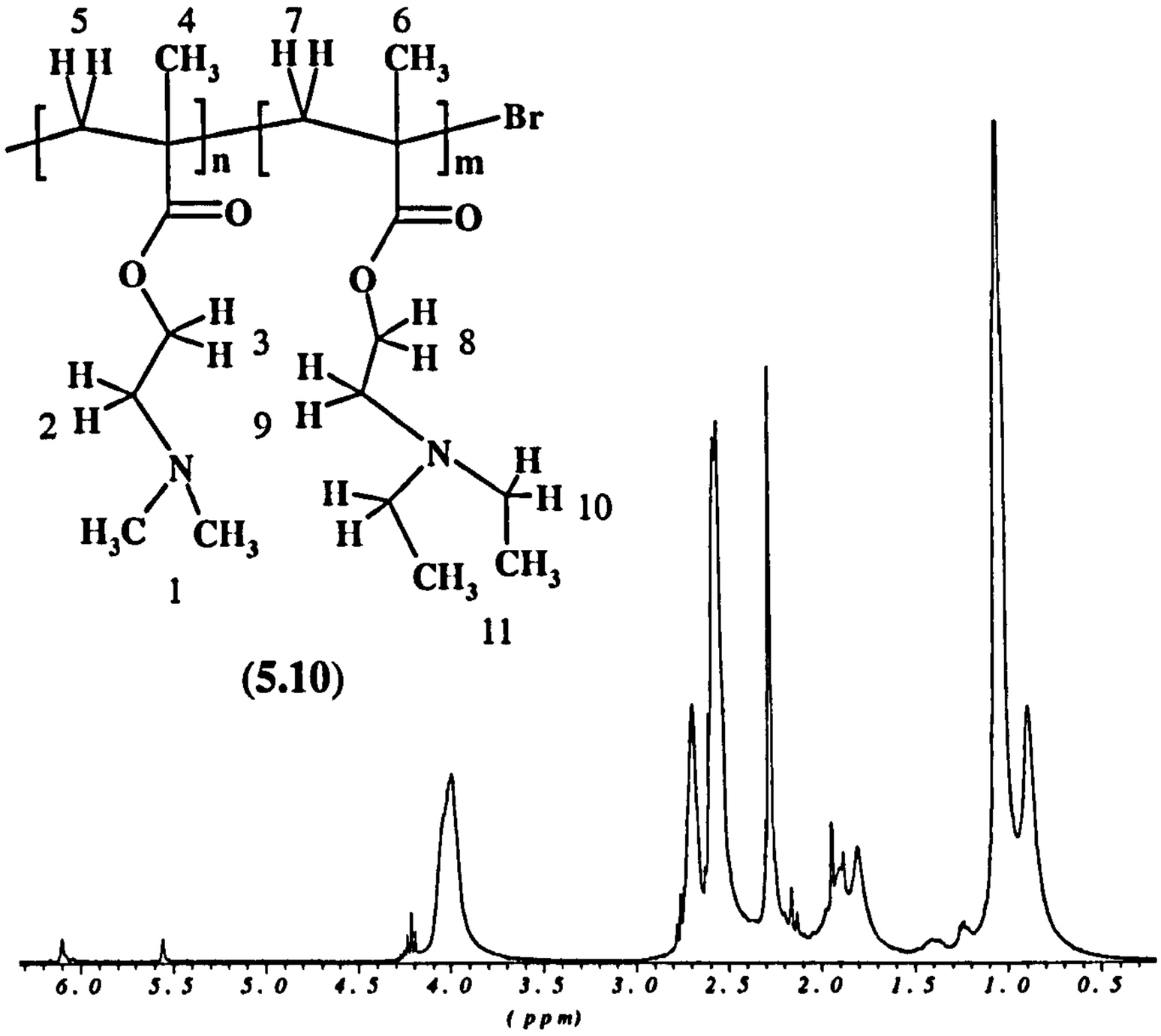


Table 5.16 **Peak assignment for the 250 MHz, ^{1}H NMR in $CDCl_3$ of PDMAEMA-co-PDEAEMA [25]:[75] statistical co-polymer (5.10) prepared in ATP in toluene at 90 °C**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
6.15	Singlet	0.05	Residual Monomer
5.52	Singlet	0.05	Residual Monomer
4.08	Singlet	2.00	H^3, H^8
2.28	Singlet	1.79	H^9
2.57	Singlet	3.19	H^2, H^{10}
2.26	Singlet	1.64	H^1
1.54	Multiplet	1.90	H^5, H^7
1.06	Multiplet	4.55	H^{11}, H^4, H^6

Table 5.17 Monomer composition of co-polymer products from the statistical co-polymerisation of DMAEMA and DEAEMA by ATP in toluene at 90° C

Theoretical			Product data*		
[DMAEMA]	[DEAEMA]	Mn	[DMAEMA] (^{1}H NMR)	[DEAEMA] (^{1}H NMR)	Mn (GPC)
[75]	[25]	25000	[65.3]	[34.7]	16200
[50]	[50]	25000	[59.0]	[41.0]	19400
[25]	[75]	25000	[23.4]	[76.6]	20000

* The monomer composition was calculated from the relative integrals for the peaks that represent H^1 (DMAEMA) and H^9 (DEAEMA). The data obtained is given in Table 5.17. Peaks are assigned based on the ^{1}H NMR of the respective homopolymers. Composition is calculated such that $H^1/6$ and $H^9/2$ give the relative concentration of DMAEMA and DEAEMA in the backbone of the polymer.

The polymer composition data show that, as the concentration of DMAEMA is increased relative to the DEAEMA content, the molecular weight decreases and the proportion of DEAEMA with respect to DMAEMA in the polymer increases compared to the expected theoretical composition.

5.1.9 Block co-polymer synthesis of DMAEMA with DEAEMA by ATP in toluene at 90 °C

Block co-polymer formation from ATP has been extensively reported in the literature [20,23,36-38]. Several examples of block co-polymer species that have one block based on an amine functional monomer, e.g. DMAEMA have been reported [21]. In all cases the amine functional block is prepared from a macro-initiating species that does not contain an amine functional repeat unit. No examples of block co-polymers from ATP that contain amine functional monomers in both blocks have been reported. The formation of block co-polymer species that contain two different amine monomers has been investigated in this body of research.

An initial PDMAEMA macro-initiator was prepared for all block co-polymer preparations. DMAEMA was selected in preference to DEAEMA to form the macro-initiating block due to the higher degree of control obtained in the respective homopolymerisation of DMAEMA by ATP. The PDMAEMA macro-initiating species was then used to initiate the polymerisation of DEAEMA by ATP to produce the block co-polymer product.

For all PDMAEMA macro-initiator preparations the polymerisation was performed using solution polymerisation with 33% solids in toluene at 90 °C. The ligand and initiator for all reactions were N-(n-pentyl)-2-pyridylmethanimine (**5.2**) and ethyl-2-bromoisobutyrate (**5.3**) respectively. The reaction conditions were determined such that at 80% conversion of monomer the final molecular weight of the product polymers would provide three different molecular weight bromine-terminated PDMAEMA macro-initiators. Table 5.18 outlines the reagent composition for each reaction.

Table 5.18 Reaction conditions for the Atom Transfer Polymerisation of DMAEMA in toluene at 90 °C to prepare PDMAEMA macro-initiator for block co-polymer preparation

Molar ratio				
Monomer MMA	**Initiator** Ethyl-2-bromoisobutyrate	**Cu(I)Br**	**Ligand** n-pentyl	**Theoretical Mn** (80% conversion)
100	0.7	1	2	18200
100	1.1	1	2	11600
100	2.3	1	2	5900

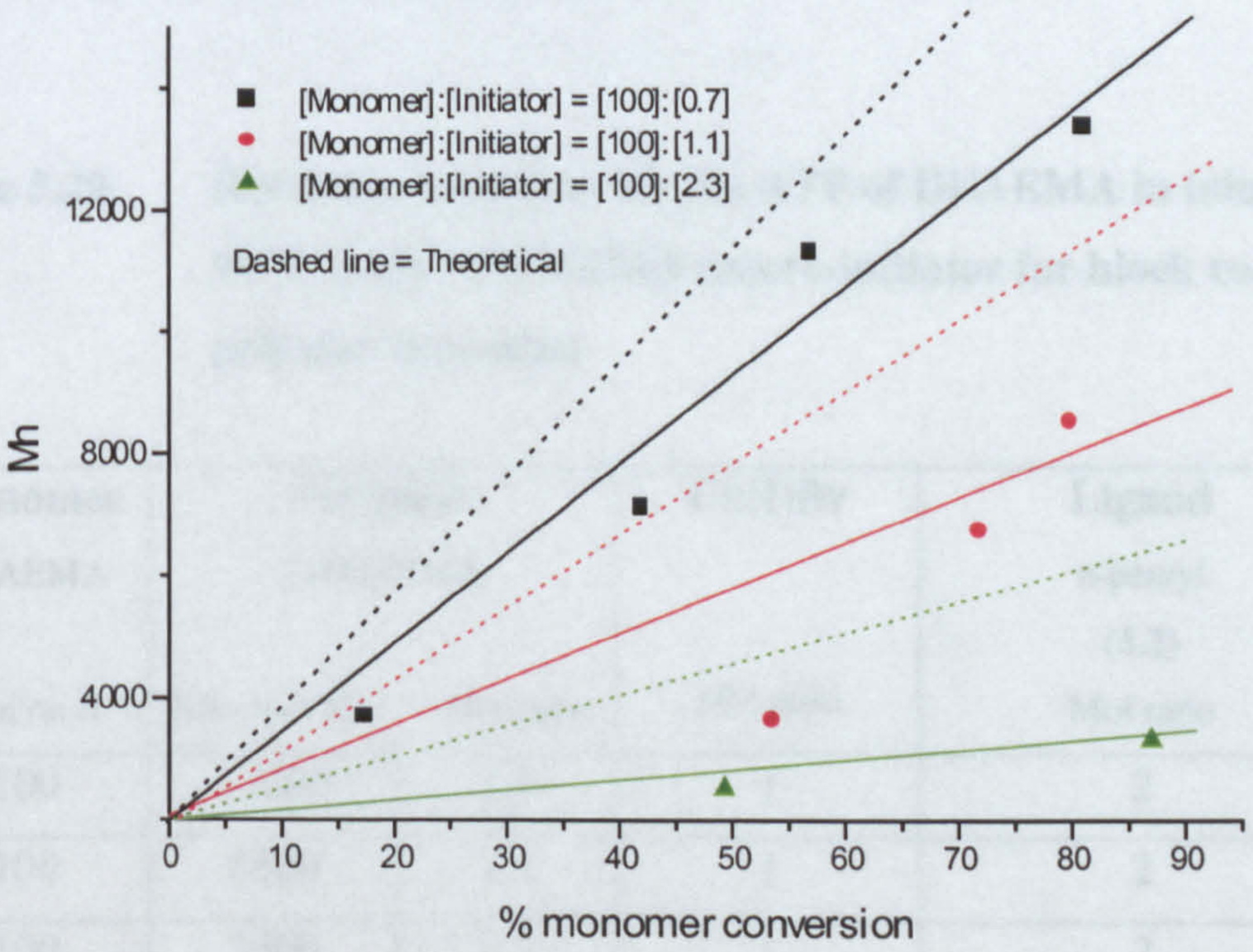
Table 5.19 lists the molecular weight and conversion data for all extracts taken from these polymerisation reactions.

Table 5.19 Molecular Weight and Conversion data for the ATP of DMAEMA in toluene at 90 °C to prepare PDMAEMA macro-initiator for block co-polymer preparation

	[M]:[I] = [100]:[0.7] (Mol ratio)			[M]:[I] = [100]:[1.1] (Mol ratio)			[M]:[I] = [100]:[2.3] (Mol ratio)		
Time (hours)	Mn	PDi	Conv (%)	Mn	PDi	Conv (%)	Mn	PDi	Conv (%)
2	3700	1.28	17.4	3600	1.23	52.1	2500	1.17	65.0
4	7100	1.30	42.1	6700	1.36	71.9	3300	1.25	87.0
5	11300	1.32	57.1	8500	1.56	80.8	-	-	-
5.5	13400	1.37	81.7	-	-	-	-	-	-

Figure 5.28 shows the plot of molecular weight versus time for each polymerisation.

Figure 5.28 Plot of Mn versus time for the ATP of DMAEMA in toluene at 90 °C to prepare PDMAEMA macro-initiator for block co-polymer preparation



The molecular weights of the polymers increased approximately linearly with reaction time. The product polymers all gave molecular weight distributions that were unimodal and typically had PDi's < 1.4. The molecular weights of the product polymers were all less than those expected by theory. The conversion data from each polymerisation showed an increase in the degree of conversion as the relative initiator concentration was raised with respect to monomer. This was expected due to the known increase in the rate of polymerisation with increasing initiator concentration as observed in section 5.1.4.

The polymer products were purified by passing through a basic alumina column to remove catalyst and by Kugelrohr distillation to remove residual monomer. Block co-polymerisation of the purified PDMAEMA homopolymers with DEAEMA by ATP was performed using solution polymerisation with 33% solids in toluene at 90°C for 6 hours. The ligand and initiator for all reactions were N-(n-pentyl)-2-pyridylmethanimine (**5.2**) and PDMAEMA macro-initiator respectively. The reaction conditions for the block co-polymerisation of the PDMAEMA macro-initiators with DEAEMA are given in Table 5.20. For each polymerisation the concentration of initiator with respect to monomer has been adjusted to give a total molecular weight of Mn = 25000 for the product co-polymer at 100% conversion of monomer.

Table 5.20 Reaction conditions for the ATP of DEAEMA in toluene at 90 °C from PDMAEMA macro-initiator for block co-polymer formation

Monomer DEAEMA Mol ratio	**Initiator** PDMAEMA Initiator (Mn)	Mol ratio	**Cu(I)Br** Mol ratio	**Ligand** n-pentyl **(5.2)** Mol ratio
100	13400	1.6	1	2
100	8500	1.1	1	2
100	3300	0.8	1	2

Table 5.21 gives the molecular weight data for the product polymers in comparison to the molecular weight of the starting macro-initiator. No polymer growth was observed for the polymerisation initiated from PDMAEMA Mn = 3300.

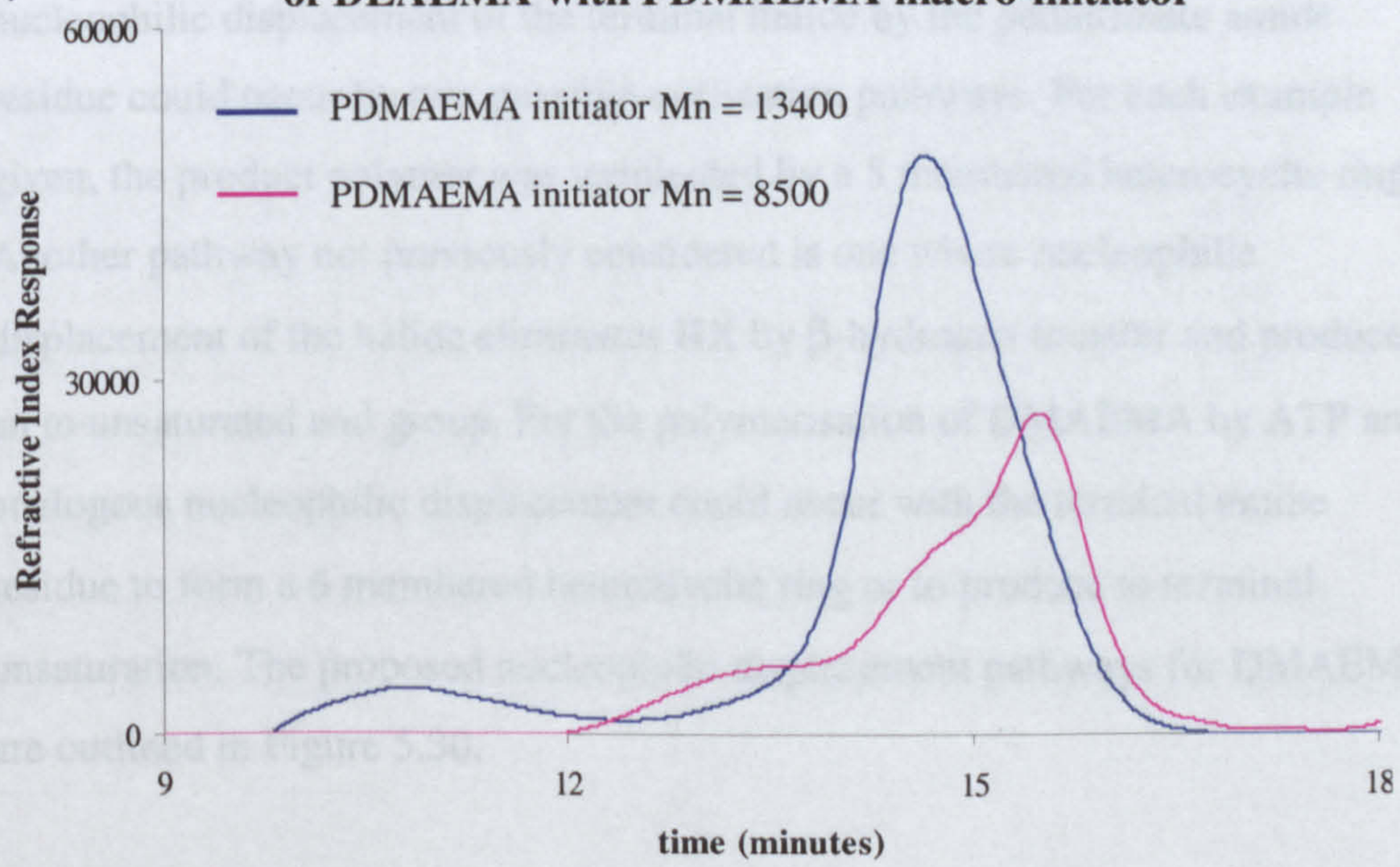
Table 5.21 Molecular Weight and conversion data for the ATP of DEAEMA in toluene at 90 °C with PDMAEMA macro-initiator for block co-polymer preparation for samples taken after 6 hours

[M]:[I]	PDMAEMA		Product analyses		
Mol ratio	Mn	PDi	Mn	PDi	Conversion (%)
[100]:[1.6]	13400	1.37	16200*	1.45*	7.1
[100]:[1.1]	8500	1.56	12100	2.77	8.6
[100]:[0.8]	3300	1.25	-	-	0.7

* Molecular weight distribution data was determined for the lower molecular weight peak for a bimodal polymer distribution obtained from GPC.

The Gel Permeation Chromatography refractive index response of the polymer component for the co-polymer obtained from PDMAEMA initiators Mn = 13400 and Mn = 8500 are given in Figure 5.29.

Figure 5.29 Gel Permeation Chromatograms of product from the ATP of DEAEMA with PDMAEMA macro-initiator

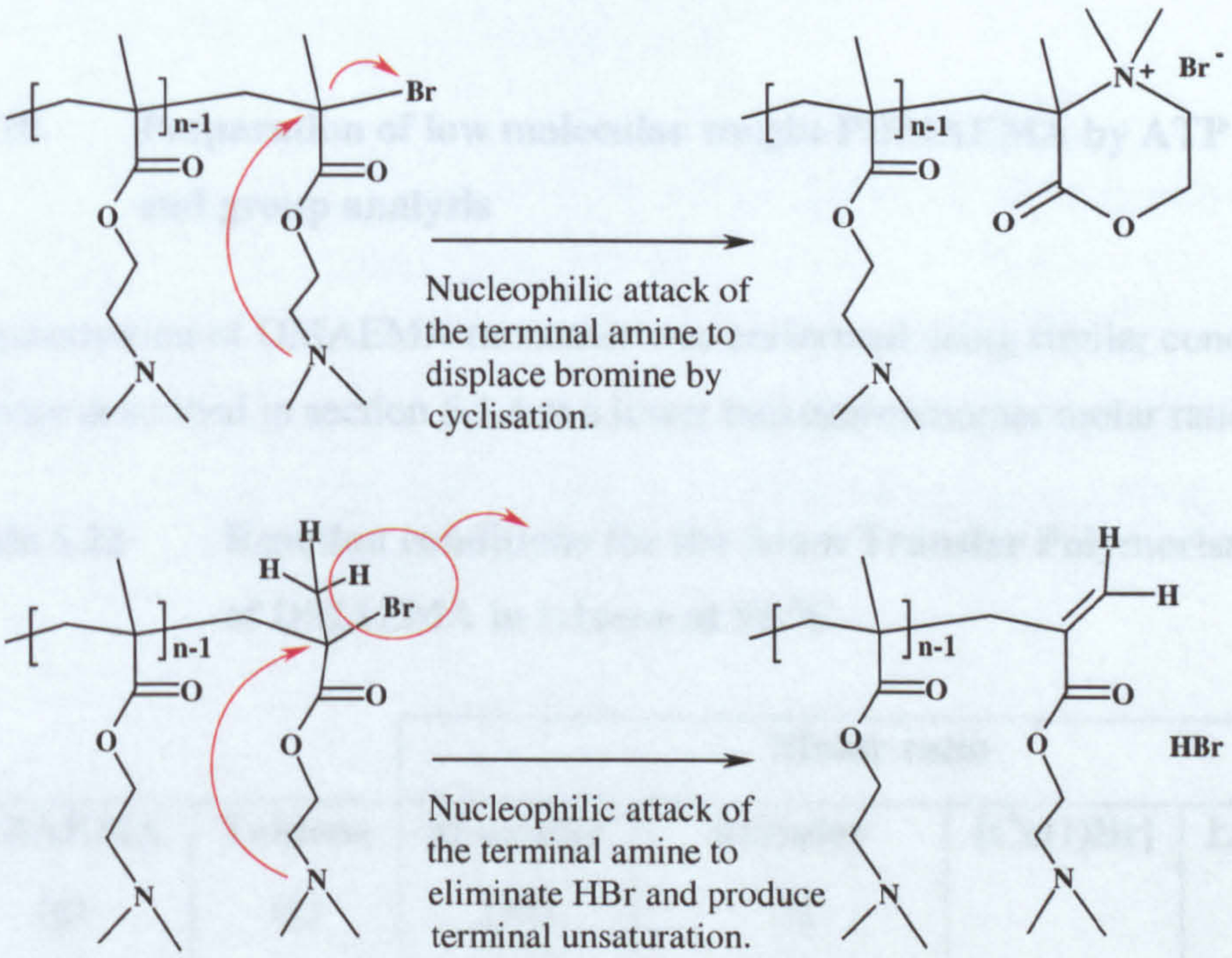


Both chromatograms exhibit bimodal distributions. The low molecular weight peak in each bimodal distribution is found at approximately the same elustion time as that for the PDMAEMA macro-initiator. The degree of conversion is low showing that only a fraction of monomer has been consumed during the polymerisation procedure.

The block co-polymerisation reaction of DEAEMA with a PDMAEMA macro-initiator was repeated several times with different PDMAEMA macro-initiators. Each product gave a broad or bimodal distribution and only a low conversion of monomer was obtained in comparison to that which was expected.

The observed bimodal distribution and broadening in the polydispersity index may result from homopolymerisation of DEAEMA monomer to produce a new two component homopolymer system. This is unlikely due to the lack of a primary radical source in the reaction and the reluctance of methacrylate monomers to self-initiate. Bimodal distributions can also be formed when a proportion of the macro-initiating species has become inactive. In this case block co-polymer is formed from those PDMAEMA macro-initiating species that are active and a degree of PDMAEMA homopolymer impurity will also be present from those species that are unable to initiate block co-polymerisation. The loss of control for amine functional monomers in ATP by self-termination reactions has been previously reported by Matyjaszewski *et al* for the polymerisation of N,N-dimethacrylamide [24]. Matyjaszewski *et al* proposed that nucleophilic displacement of the terminal halide by the penultimate amide residue could occur by two possible cyclisation pathways. For each example given, the product polymer was terminated by a 5 membered heterocyclic ring. Another pathway not previously considered is one where nucleophilic displacement of the halide eliminates HX by β-hydrogen transfer and produces an ω-unsaturated end group. For the polymerisation of DMAEMA by ATP an analogous nucleophilic displacement could occur with the terminal amine residue to form a 6 membered heterocyclic ring or to produce ω-terminal unsaturation. The proposed nucleophilic displacement pathways for DMAEMA are outlined in Figure 5.30.

Figure 5.30 Possible nucleophilic displacement of the terminal halide species in ATP reactions of DMAEMA



A reduction in the degree of initiation of the PDMAEMA homopolymer might be the result of nucleophilic displacement or as a result of the purification procedure for the PDMAEMA macro-initiator. The purification of the macro-initiator by reduced pressure distillation is a harsh procedure compared with standard precipitation processes, due to the lack of a non-solvent for the polymer in comparison to the monomer. Dialysis equilibration is not possible with standard dialysis membranes due to the high degree of affinity of the polymer and monomer with the membrane surface.

The lack of controlled polymerisation for N,N-dimethacrylamide leads to broadening in the polydispersity index of the homopolymer and a large reduction in the apparent rate of polymerisation. The polymerisation of DMAEMA by ATP was shown in section 5.1.4 to provide good control with a comparable rate of polymerisation to that found for ATP of MMA. These factors indicate that if nucleophilic displacement of the terminal halide functionality occurs then the displacement reaction is much slower than for N,N-dimethacrylamide. To investigate the nature of the end-group functionality

of the PDMAEMA macro-initiator after purification a low molecular weight PDMAEMA homopolymer was prepared using ATP.

5.1.10 Preparation of low molecular weight PDMAEMA by ATP for end group analysis

Polymerisation of DMAEMA monomer was performed using similar conditions to those described in section 5.1.4 at a lower initiator/monomer molar ratio.

Table 5.22 Reaction conditions for the Atom Transfer Polymerisation of DMAEMA in toluene at 90 °C

		Molar ratio			
DMAEMA (g)	**Toluene (g)**	**Monomer [M] MMA**	**Initiator [I] Ethyl-2-bromoisobutyrate**	**[Cu(I)Br]**	**Ligand [L] n-pentyl**
2	4	100	4.5	1	2

Table 5.23 lists the molecular weight and conversion data obtained by gravimetry from the extracts of the reaction where [Monomer]:[Initiator] = [100]:[4.5].

Table 5.23 Molecular weight and conversion data for ATP of DMAEMA with [Monomer]:[Initiator] = [100]:[4.5] in toluene at 90 °C

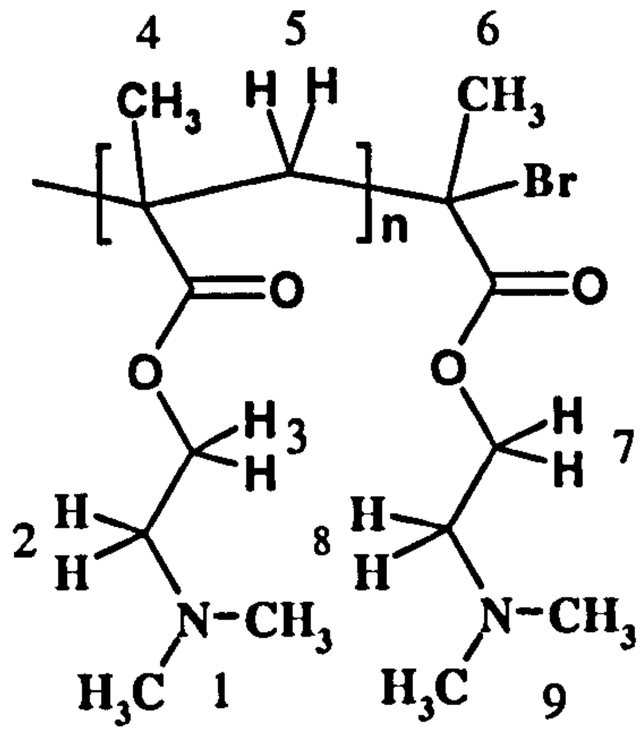
Sample (hours)	**Mn**	**PDi**	**Conversion (%)**	**Theoretical Mn**
2	1300	1.25	45.2	1600
3	1800	1.34	59.3	2100
4	1800	1.35	60.6	2100
5	1900	1.35	62.7	2200

The product polymer was purified by passing through a column of activated basic alumina and then residual monomer was removed by reduced pressure

distillation. A high resolution 300 MHz, ^{1}H NMR spectrum of the polymer was obtained with multiple scans to determine the end group functionality of the PDMAEMA homopolymer after purification.

The 300 MHz, ^{1}H NMR spectrum of the purified PDMAEMA homopolymer **(5.12)**, Mn = 1900 is given in Figure 5.31.

Figure 5.31 **300 MHz, ^{1}H NMR in $CDCl_3$ of low Mn, PDMAEMA homopolymer (5.12) Mn = 1900, prepared in ATP in toluene at 90 °C**



(5.12)

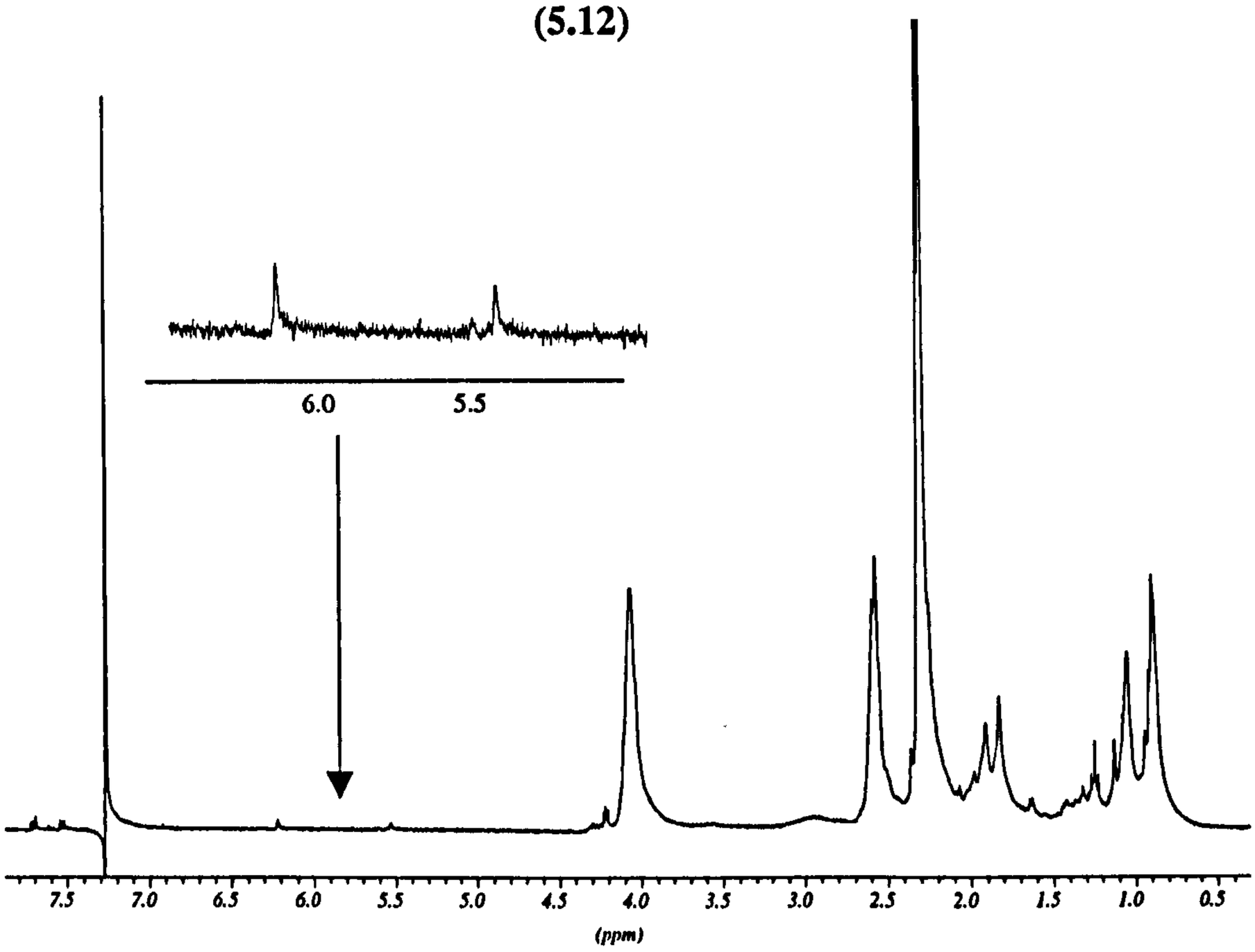


Table 5.24 Peak assignment for the 300 MHz, ^1H NMR in $CDCl_3$ of low Mn, PDMAEMA (5.12) from ATP in toluene at 90 °C

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
7.27	Singlet	-	Solvent, $CDCl_3$
6.22	Singlet	0.01	Vinyl proton
5.53	Singlet	0.01	Vinyl proton
4.07	Singlet	1.00	H^2, H^8
2.91	Singlet	0.10	-
2.57	Multiplet	1.00	H^3, H^7
2.29	Singlet	2.94	H^1, H^9
1.91	Multiplet	0.99	H^5
1.05	Multiplet	2.06	H^4, H^6

The proton signal for the methoxy functionality α to the terminal bromine in PMMA is located at 3.82 ppm in deuterated chloroform. The 300 MHz, ^1H NMR spectrum of the PDMAEMA homopolymer (**5.12**) from the reaction where [Monomer]:[Initiator] = [100]:[4.5] after 5 hours does not exhibit a defined signal for the O-CH_2-R protons (H^7) α to the bromine. Unlike the corresponding analysis of higher molecular weight PDMAEMA homopolymer from ATP (**5.6**) in section 5.1.4, the low molecular weight product shows an unassigned broad singlet at 2.91 ppm and two singlets that represent vinylic protons at 6.62 and 5.53 ppm. The peaks assigned as vinylic protons fall in the same region as those for DMAEMA monomer and PDMAEMA macromonomer (**3.1**) prepared by catalytic chain transfer polymerisation. These peaks may correspond to residual monomer impurities or those from terminal unsaturation of the polymer product. Each sample was vacuum distilled to constant pressure before analysis and GPC analysis of the distilled product showed no monomer impurity.

No conclusive evidence has been found to support the presence of bromine terminated polymer from these studies and the peak broadening in the NMR of the polymer species prevents accurate identification of the end group functionality. The bimodal distribution of polymers that are obtained from the ATP of a co-monomer species with PDMAEMA macro-initiators suggests that partial elimination of the Br end group has occurred after the reaction was terminated. The broad singlet at 2.91 ppm is not assigned, however this may be due to the presence of the dimethyl protons at the quaternary centre resulting from cyclisation reactions.

Further work is required for the analysis of low molecular weight PDMAEMA homopolymer prepared by ATP for end group analysis. It was not in the scope of this body of research to examine the mechanistic features of these reactions. Instead, work has concentrated on the polymerisation of DMAEMA with DEAEMA to produce gradient co-polymers from ATP that can be functionalised to form gradient co-polymers with selective quaternisation.

5.1.11 Preparation of PDMAEMA-co-PDEAEMA gradient co-polymers by ATP in toluene at 90 °C

Gradient co-polymerisation of DMAEMA monomer with DEAEMA was performed using ATP in toluene at 90 °C. A gradient co-polymer is one that contains a gradient in monomer distribution. Figure 5.32 illustrates in schematic terms an A-B gradient co-polymer.

Figure 5.32 A-B Gradient co-polymer

A-A-A-A-A-A-A-B-A-A-B-B-A-B-B-B-A-B-B-B-B-B-B-B

A-B gradient co-polymers can be formed from ATP by the initial homopolymerisation of monomer A to give approximately 80% monomer conversion and then the direct addition of monomer B to the propagating reaction. A gradient co-polymer is formed that contains a discrete block of

monomer A, with the second block containing a statistical distribution of A and B. A gradient in the distribution of monomer in the co-polymer block can result from differences in the relative reactivity ratios of the two component monomers.

A series of gradient co-polymers were prepared using ATP of DMAEMA and DEAEMA. For all reactions the polymerisation of DMAEMA was performed first via solution polymerisation at 33% solids in toluene at 90 °C. The ligand and initiator for all reactions were N-(n-pentyl)-2-pyridylmethanimine (**5.2**) and ethyl-2-bromoisobutyrate (**5.3**) respectively. The DEAEMA monomer was added when the DMAEMA monomer conversion was approximately 80%. The reactions conditions were determined such that at 100% conversion of both monomers the final molecular weight of the product polymer would be 25000 Da. Table 5.25 outlines the reaction conditions for each reaction.

Table 5.25 Reaction conditions for the Atom Transfer gradient co-Polymerisation of DMAEMA with DEAEMA in toluene at 90 °C

Monomer M^1 DMAEMA	**Monomer M^2** DEAEMA	**Total Monomer M^{1+2}**	**Initiator** Ethyl-2-bromoisobutyrate **(5.3)**	**Cu(I)Br**	**Ligand** n-pentyl **(5.2)**
100	33	133	0.87	1	2
100	100	200	1.37	1	2
100	300	400	2.85	1	2
100	900	1000	7.30	1	2

Tables 5.26 and 5.27 list some of the molecular weight and the conversion data for the polymerisations. Conversion data is calculated based on the instantaneous conversion of both monomers at the time of sampling. A sample was always taken from the reaction immediately prior to the addition of M^2 to give an accurate conversion of M^1 prior to gradient co-polymerisation.

Table 5.26 Molecular weight and conversion data for ATP of DMAEMA and DEAEMA where DMAEMA = Monomer 1 and [Monomer 1]:[Initiator] = [100]:[2.85] in toluene at 90 °C

Sample (hours)	Mn	PDi	Conversion (%)	Theoretical Mn*
0	Monomer 1 [DMAEMA] added			
2	900	1.25	29.6	1700
4	3900	1.72	73.9	4200
4	Monomer 2 [DEAEMA] added			
12	18700	1.79	88.4	21100

* The theoretical Mn values are calculated using equation 1.8 from chapter 1 section 1.5.2.

Table 5.27 Conversion data for the gradient co-polymerisation by ATP of DMAEMA and DEAEMA in toluene at 90 °C

	Instantaneous Monomer Conversion Data (%)			
Sample (hours)	$[M^1]$:[I] [100]:[0.87]	$[M^1]$:[I] [100]:[1.37]	$[M^1]$:[I] [100]:[2.85]	$[M^1]$:[I] [100]:[7.3]
2	15.2	39.3	29.6	31.1
4	-	-	73.9, [add M^2]	41.1 add [M^2]
5	-	86.7, add [M^2]	-	-
5.5	89.3, add [M^2]	-	-	71.9
12	100	100	88.4	98.6

The conversion data show that for the reaction where $[M^1]$:[I] = [100]:[7.3], monomer conversion of M^1 only reaches 41%. All other reactions show conversions above 78% and below 90%, this represents a suitable range for gradient co-polymerisation. The unexpectedly low conversion data from the

reaction where $[M^1]$:[I] = [100]:[7.3] maybe due to the introduction of oxygen into the system during sampling.

A plot of increase in molecular weight versus the total % monomer conversion $[M^1] + [M^2]$ is given for each reaction in Figure 5.33.

Figure 5.33 Plot of Mn versus time for the preparation of gradient co-polymer from ATP of DMAEMA with DEAEMA in toluene at 90 °C

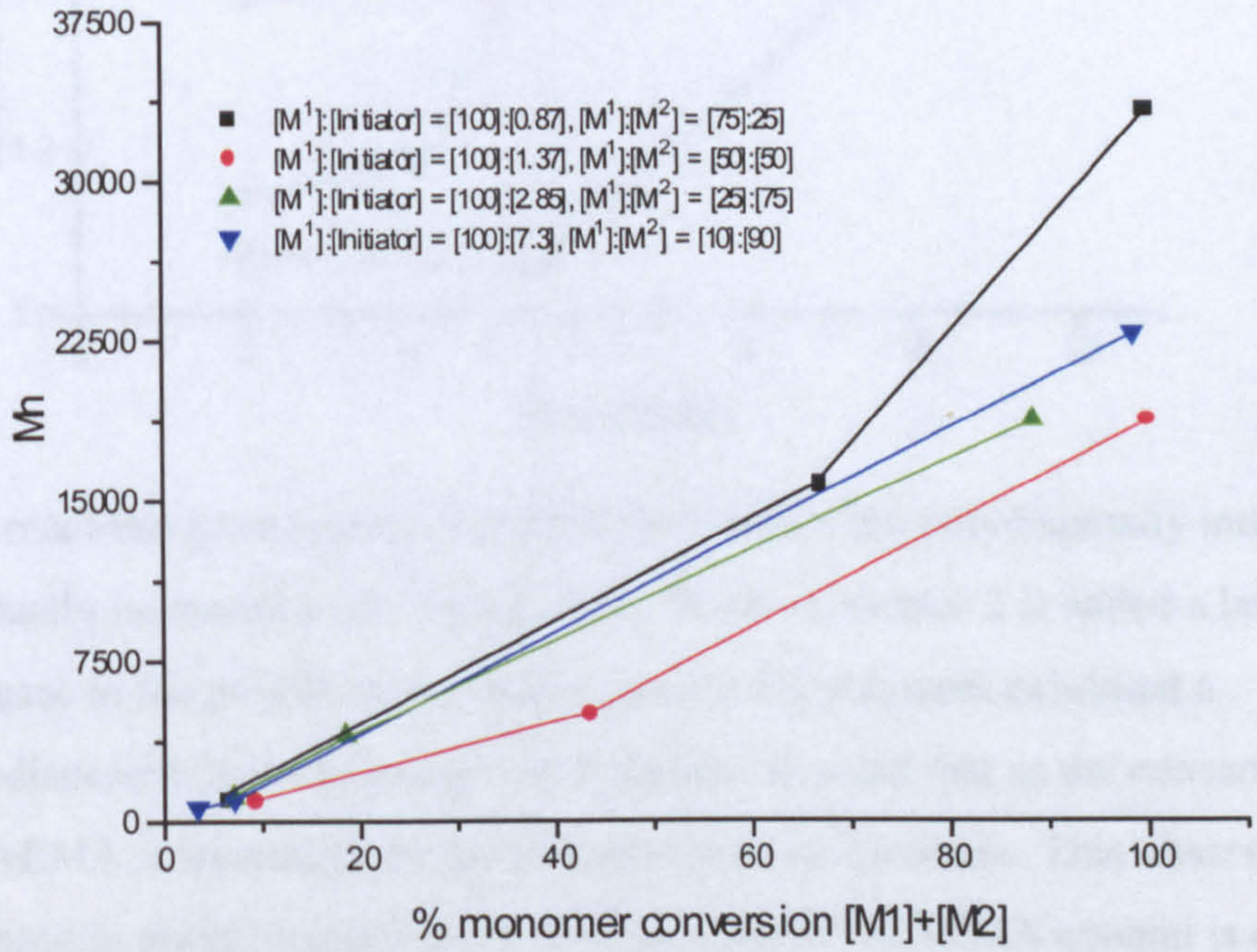
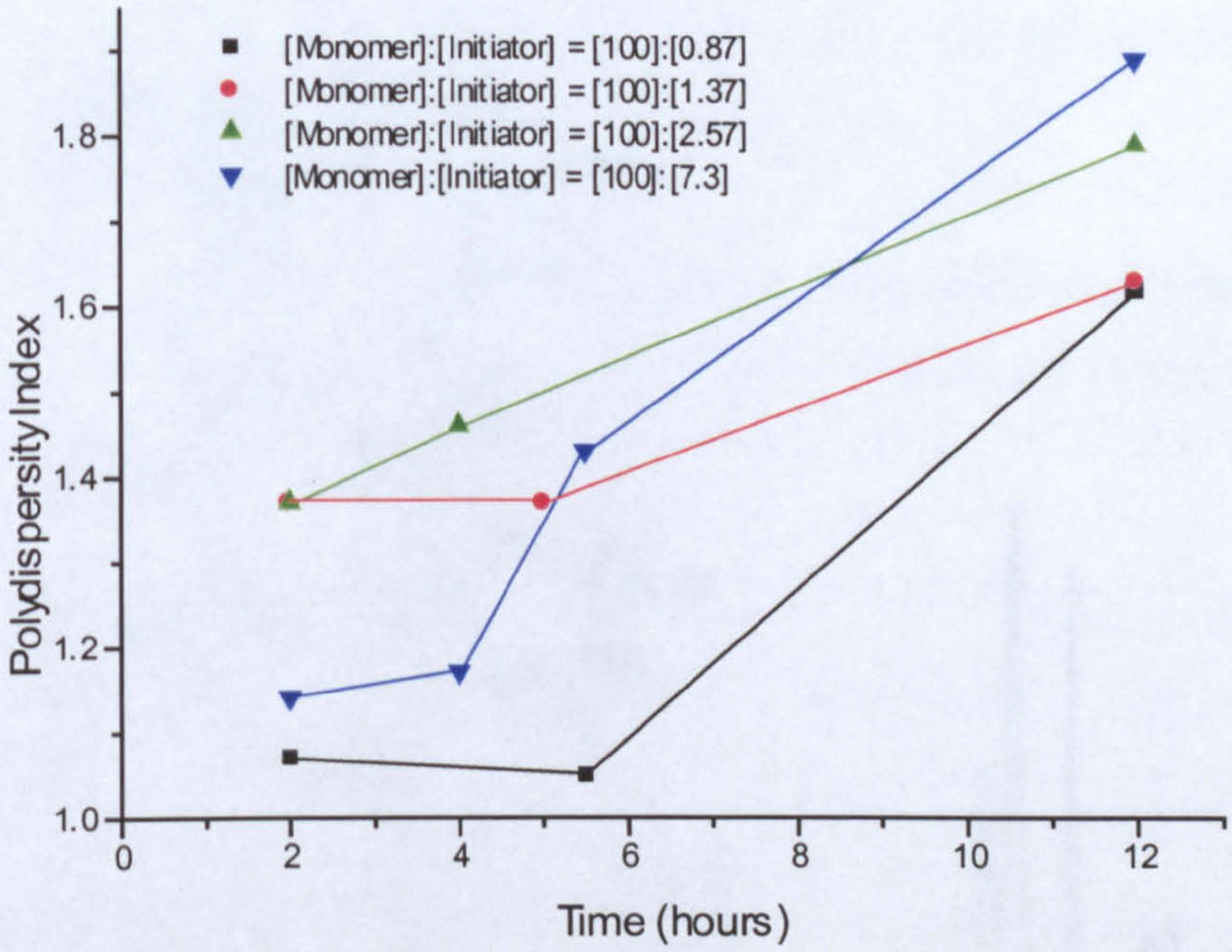


Figure 5.33 shows that the experimental evolution of the molecular weight with conversion is in good agreement with the predicted molecular weight from theory, this supports the conclusion that gradient co-polymerisation has been successful. There does not appear to be any trend in the data resulting from monomer composition. The molecular weights of the product polymers are all greater than 18000 $g.mol^{-1}$ and less than 34000 $g.mol^{-1}$.

Figure 5.34 shows the change in polydispersity index for the polymerisations as a function of reaction time.

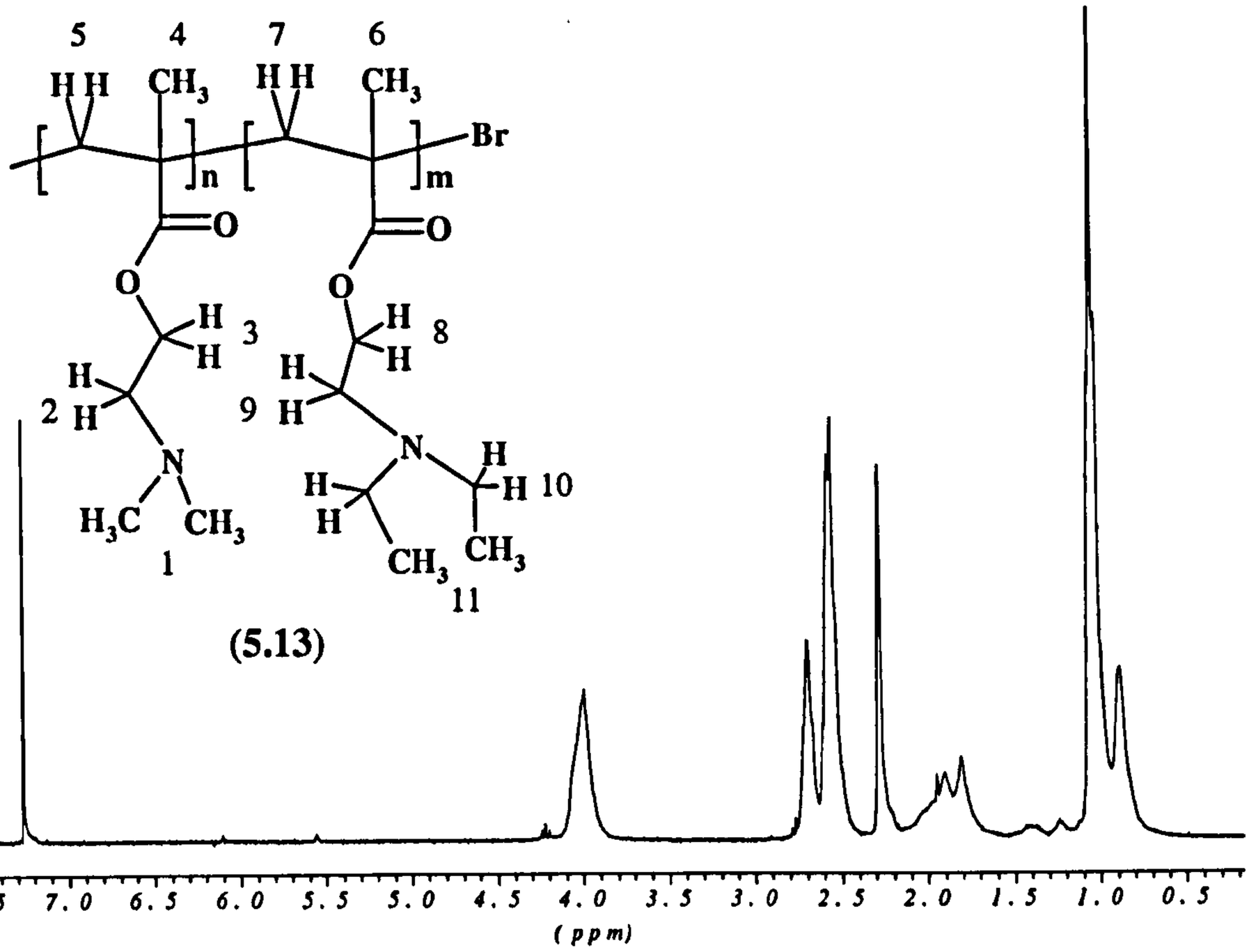
Figure 5.34 Plot of Polydispersity Index (PDi) versus time for the gradient co-polymerisation of DMAEMA and DEAEMA by ATP in toluene at 90 °C



The reactions gave unimodal distributions where the polydispersity index gradually increased with reaction time. When monomer 2 is added a large increase in the polydispersity index occurs. All polymers exhibited a polydispersity index less than 1.9. It should be noted that as the concentration of DEAEMA is increased, the polydispersity index increases. This observed increase in polydispersity index with increase in DEAEMA content is expected due to the apparent reduction in the degree of control obtained for DEAEMA in comparison to DMAEMA for the corresponding homopolymerisation by ATP of each monomer. The product with the highest polydispersity index is that from the reaction where low conversion was observed when monomer 2 was added and therefore maybe the result of undesired termination reactions.

The products were analysed by ^{1}H NMR spectroscopy to determine the monomer composition. The ^{1}H NMR for the sample where Monomer 1 was DMAEMA and where Monomer 2 was DEAEMA and the relative concentration of $[M^{1}]$:$[M^{2}]$ was [25]:[75] is given in figure 5.35.

Figure 5.35 **250 MHz, ^{1}H NMR in $CDCl_3$ of [PDMAEMA]:[PDEAEMA] [25]:[75] gradient co-polymer (5.13) Mn = 18700 g.mol^{-1} prepared in ATP in toluene at 90 °C**



(5.13)

Table 5.28 **Peak assignment for the 250 MHz, ^{1}H NMR in $CDCl_3$ of PDMAEMA-co-PDEAEMA [25]:[75] gradient co-polymer (5.13) Mn =18700 g.mol^{-1}, prepared in ATP in toluene at 90 °C**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
7.27	Singlet	-	Solvent, $CDCl_3$
6.11	Singlet	0.01	Monomer
5.56	Singlet	0.01	Monomer
3.99	Singlet	1.00	H^3, H^8
2.69	Singlet	0.67	H^9
2.57	Singlet	1.81	H^2, H^{10}
2.35	Singlet	0.69	H^1
1.81	Multiplet	1.03	H^5, H^7
1.02	Multiplet	3.66	H^{11}, H^4, H^6

The monomer composition was calculated from the relative integrals for the peaks that represent H^1 (DMAEMA) and H^9 (DEAEMA). The data obtained is given in Table 5.29. The peaks that are assigned as monomer may also be due to the elimination of the Br termini by nucleophilic displacement to produce an unsaturated product as described in Figure 5.30.

Table 5.29 Monomer composition of co-polymer products from the gradient co-polymerisation of DMAEMA and DEAEMA by ATP in toluene at 90° C

Theoretical			Product data		
DMAEMA	DEAEMA	Mn	DMAEMA (^{1}H NMR) %	DEAEMA (^{1}H NMR) %	Mn (GPC)
75	25	25000	63.0	37.0	33300
50	50	25000	35.7	64.3	18700
25	75	25000	33.0	67.0	18700
10	90	25000	10.3	89.7	22800

The data from ^{1}H NMR showed that the monomer composition was in good agreement with the theoretical values. A degree of error was noted for samples where the DMAEMA concentration was higher. As with the synthesis of the low molecular weight homopolymer of DMAEMA a small degree of vinyl group impurity was found to be present in the sample. These vinyl peaks were not observed in the ^{1}H NMR analyses of all gradient co-polymer products. Therefore these peaks are attributed to residual monomer.

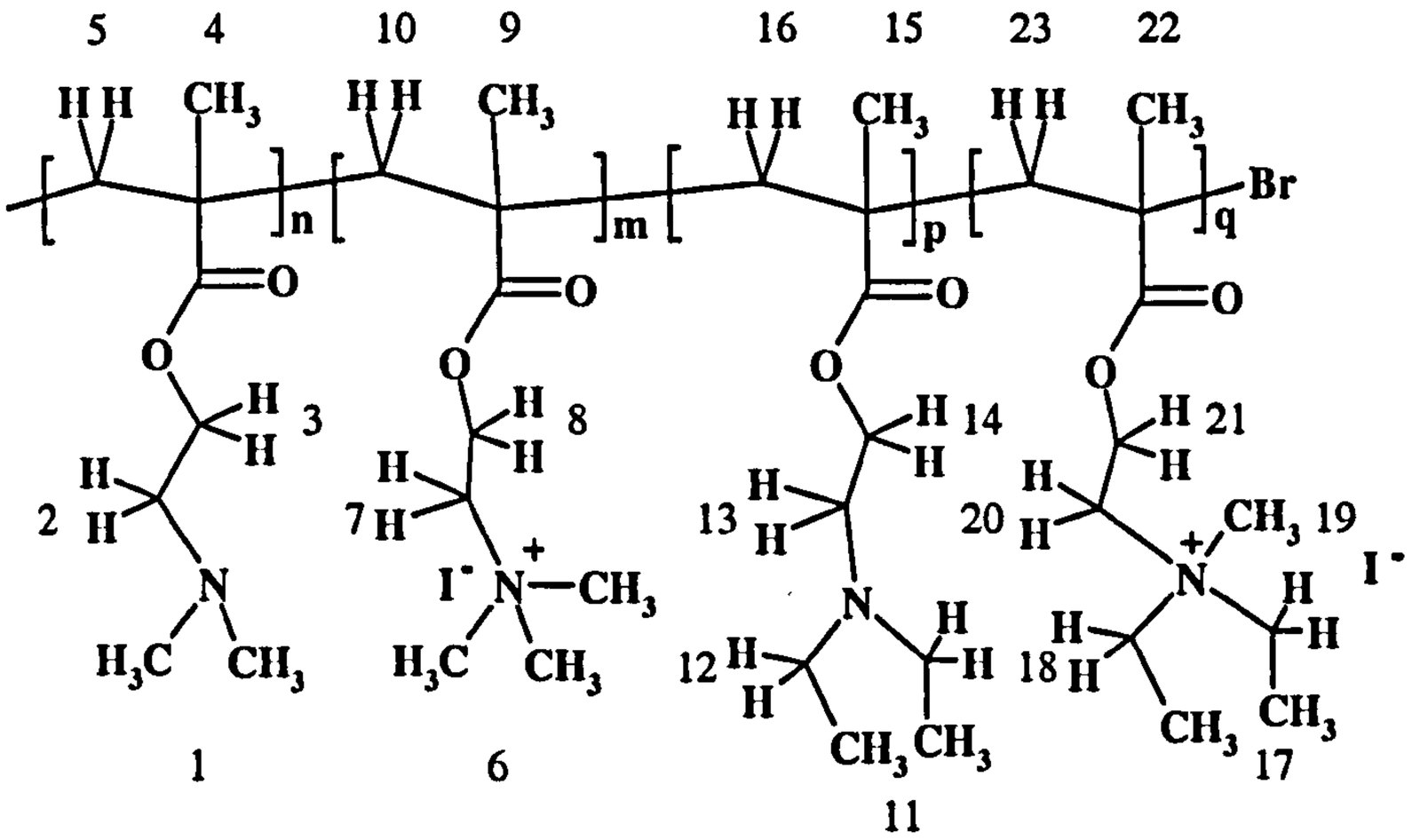
The conversion data of the products from the gradient co-polymerisation showed that molecular weight increased during polymerisation. The GPC analyses of the products showed that each product gave a unimodal distribution.

5.1.12 Selective quaternisation of PDMAEMA-co-PDEAEMA gradient co-polymer species prepared in 5.1.11

A series of reactions were performed to quaternise the gradient co-polymer products described in section 5.1.11 to determine whether selective quaternisation of the PDMAEMA residue was possible. All quaternisation reactions were performed with the addition of methyl iodide. These reactions were analogous to those performed with the PDMAEMA homopolymer in chapter 2 to produce statistical co-polymer products. All quaternisation reactions were performed in THF solution at room temperature for 24 hours.

The general structure for the quaternisation products from these reactions is given in Figure 5.36. For each product the ratio of m, n, p and q varies depending on the concentration of methyl iodide added and the degree of selective quaternisation achieved. Where completely selective quaternisation of PDMAEMA is attained then q = 0.

Figure 5.36 General structure for the products from the quaternisation of PDMAEMA-co-PDEAEMA gradient co-polymer with methyl iodide (5.14)



(5.14)

Table 5.30 lists the quaternisation reactions performed with each polymer in terms of the percentage of quaternisation with respect to [DMAEMA] in the co-polymer and with respect to the total amine residue in the co-polymer product.

Table 5.30 Reaction compositions for the quaternisation of PDMAEMA-co-PDEAEMA gradient co-polymers with MeI

[DMAEMA]:[DEAEMA] gradient co-polymer	[MeI]	% quaternisation with respect to [DMAEMA]	% quaternisation with respect to [DMAEMA]+[DEAEMA]
[63]:[37]	[63]	100	63
[63]:[37]	[37.8]	60	37.8
[63]:[37]	[12.6]	20	12.6
[35.7]:[64.3]	[35.7]	100	35.7
[35.7]:[64.3]	[21.4]	60	21.4
[35.7]:[64.3]	[7.2]	20	7.2
[10.3]:[89.7]	[10.3]	100	10.3
[10.3]:[89.7]	[6.2]	60	6.2
[10.3]:[89.7]	[2.0]	20	2.0

The products were analysed by ^{1}H NMR spectroscopy to determine the degree of selective quaternisation obtained. The ^{1}H NMR for the sample where [DMAEMA]:[DEAEMA] was [35.7]:[64.3] is given in Figure 5.37 for the sample with 100% quaternisation with respect to [DMAEMA]. The ^{1}H NMR for the sample where [DMAEMA]:[DEAEMA] was [63]:[37] is given in Figure 5.38 for the sample with 60% quaternisation with respect to [DMAEMA].

Figure 5.37 **250 MHz, ^{1}H NMR in D_2O of quaternised PDMAEMA-co-PDEAEMA gradient co-polymer (5.14) where [DMAEMA]:[DEAEMA] = [35.7]:[64.3] with 100% quaternisation with respect to [DMAEMA]**

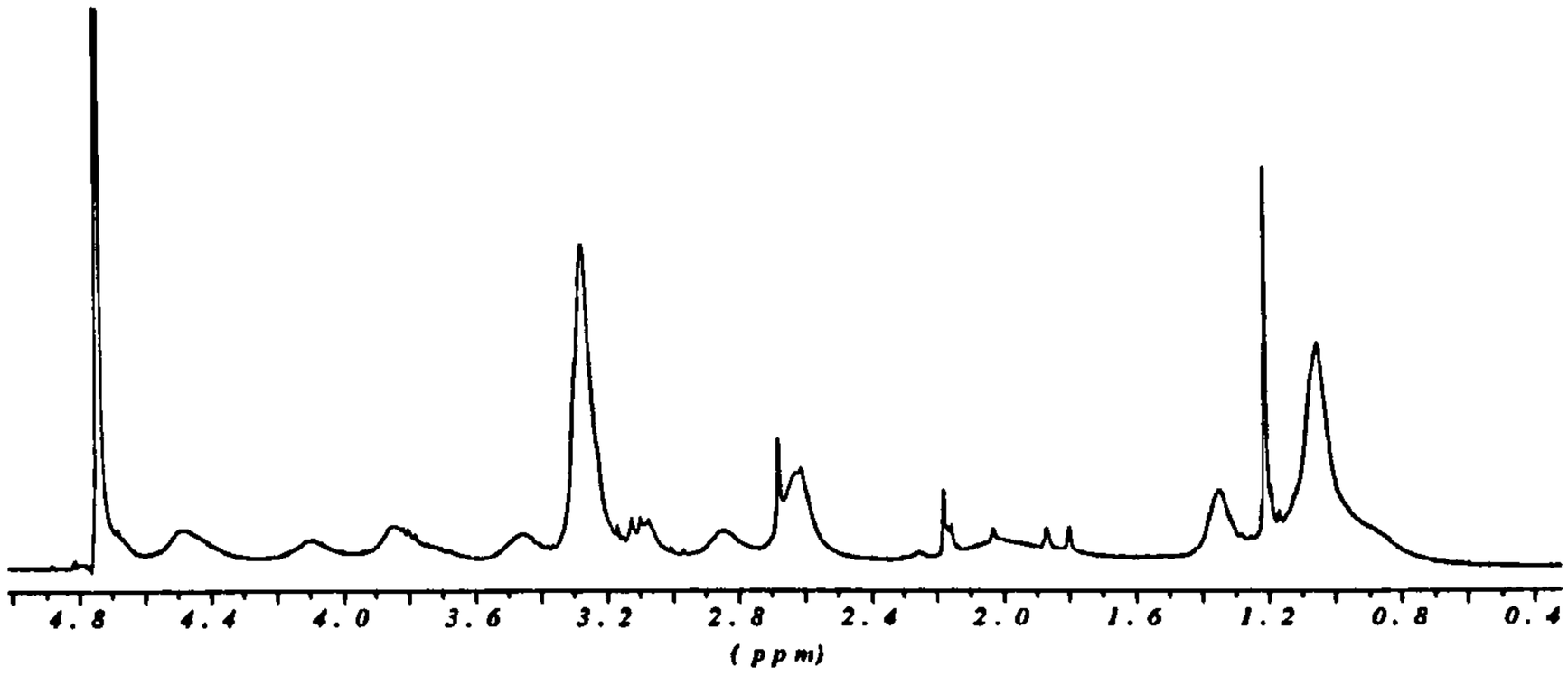


Table 5.31 **Peak assignment for the 250 MHz, ^{1}H NMR in D_2O of quaternised PDMAEMA-co-PDEAEMA gradient co-polymer (5.14) prepared from [DMAEMA]:[DEAEMA] = [35.7]:[64.3] with 100% quaternisation with respect to [DMAEMA]**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
4.70	Singlet	-	Solvent, D_2O
4.43	Singlet	0.62	H^8, H^{21}
4.06	Singlet	0.32	H^3, H^{14}
3.80	Multiplet	0.77	H^7
3.43	Singlet	0.33	H^{20}
3.23	Singlet	2.91	H^6
3.02	Multiplet	0.65	H^{19}
2.80	Singlet	0.57	H^{18}
2.61	Singlet	1.81	H^2, H^{12}, H^{13}
2.20	Singlet	0.23	H^1
1.98	Multiplet	1.65	H^5, H^{10}, H^{16}, H^{23}
1.35	Singlet	0.89	H^{17}
1.16	Singlet	0.63	H^{11}
1.05	Multiplet	3.65	H^4, H^9, H^{15}, H^{22}

The spectrum analysis for the sample where methyl iodide was added to give 100% quaternisation with respect to the [DMAEMA] showed that partial quaternisation of the DMAEMA residues occurred. A degree of DMAEMA residues were shown to remain as the tertiary amine and a degree of quaternisation of the DEAEMA residues was shown to occur. A broad singlet at ~1.24 ppm was assigned as the diethylamino protons, H^{17} from the quaternised DEAEMA residue. This peak was detected only for the samples where 100% methyl iodide was added with respect to [DMAEMA]. The complexity of the spectra due to peak overlap prevents the quantitative determination of the degree of quaternisation obtained for DMAEMA and DEAEMA residues. It has been shown that selective quaternisation of the DMAEMA residues has not been achieved.

Figure 5.38 250 MHz, ^1H NMR in D_2O of quaternised PDMAEMA-co-PDEAEMA gradient co-polymer (5.14) where [DMAEMA]:[DEAEMA] = [63]:[37] with 60% quaternisation with respect to [DMAEMA]

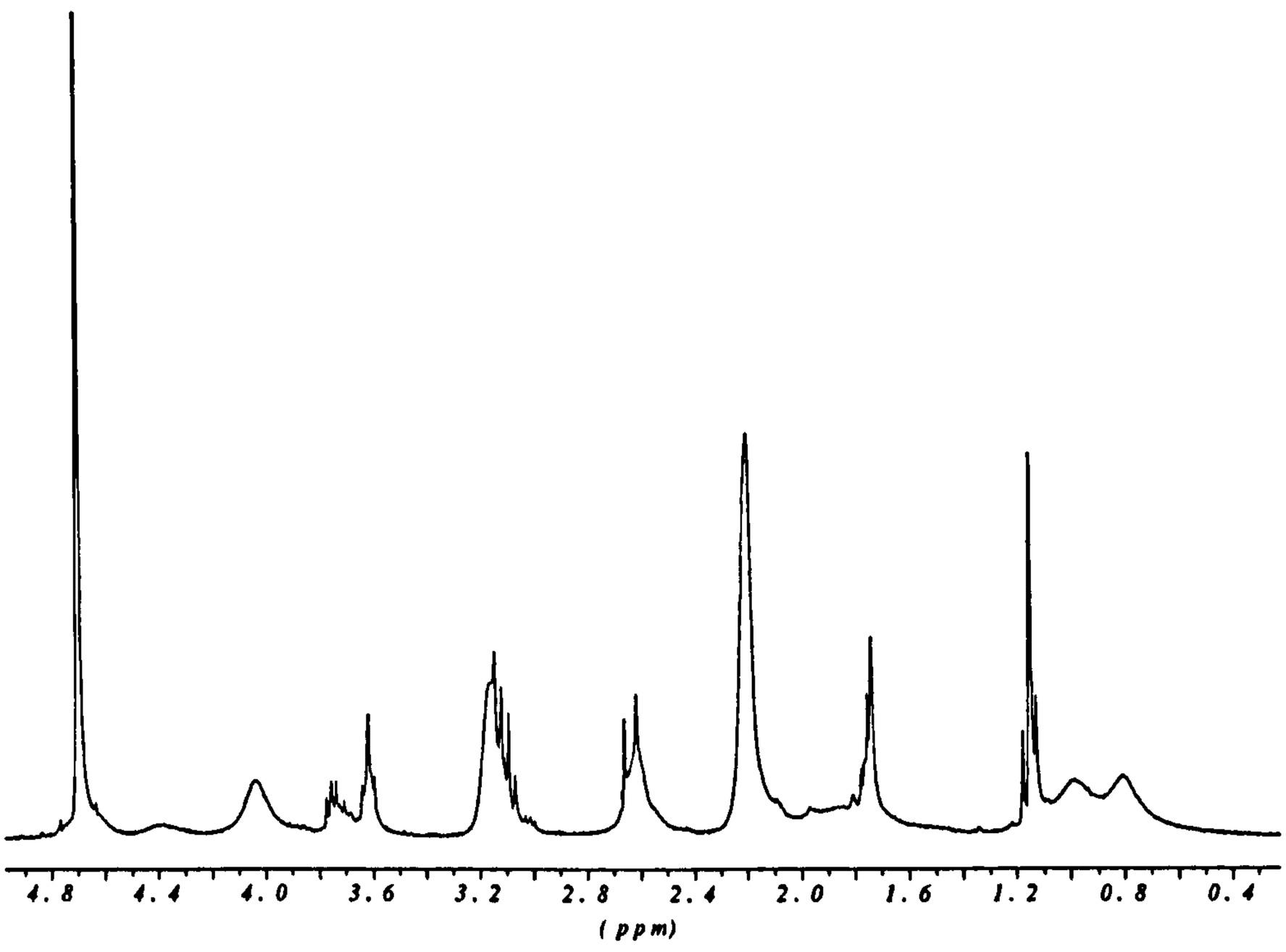


Table 5.32 **Peak assignment for the 250 MHz, ^{1}H NMR in D_2O of quaternised PDMAEMA-co-PDEAEMA gradient co-polymer (5.14) prepared from [DMAEMA]:[DEAEMA] = [63]:[37] with 60% quaternisation with respect to [DMAEMA]**

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
4.70	Singlet	-	Solvent, D_2O
4.39	Singlet	0.72	H^8
4.04	Singlet	2.29	H^3, H^{14}
3.62	Multiplet	1.49	H^7
3.14	Multiplet	6.66	H^6
2.61	Multiplet	4.34	H^2, H^{12}, H^{13}
2.20	Singlet	10.30	H^1
1.74	Multiplet	4.00	H^5, H^{10}, H^{16}
1.15	Multiplet	2.68	H^{11}
0.80	Multiplet	5.66	H^4, H^9, H^{15}

The ^{1}H NMR spectrum for the samples where methyl iodide was added to give 60% and 20% quaternisation with respect to DMAEMA residues showed that partial quaternisation of the DMAEMA residue was successfully performed. No peak was detected at ~1.24 ppm for the diethylamino protons, H^{17} from the quaternised DEAEMA residue and therefore no evidence for the quaternisation of the DEAEMA residues was found.

The data showed that selective quaternisation of the DMAEMA residues was achieved where the concentration of methyl iodide was added at 60% and 20% with respect to [DMAEMA]. When the concentration of methyl iodide was increased to 100% with respect to [DMAEMA] then only partial quaternisation was obtained and a degree of quaternisation of the DEAEMA residues was observed. The loss of selective quaternisation at high concentrations of methyl iodide is proposed to result from the increased electrostatic repulsion between quaternary repeat units.

5.2 CONCLUSIONS

The polymerisation of MMA, BzMA, DMAEMA and DEAEMA by ATP has successfully been performed. The block co-polymerisation of the BzMA polymer with DMAEMA followed by hydrolysis to produce PMAA-block-PDMAEMA was not performed due to the poor dye-binding results obtained for the analogous block co-polymers whose synthesis was outlined in Chapter 4 by catalytic chain transfer polymerisation.

The attempted block co-polymerisation of PDMAEMA with DEAEMA was unsuccessful. It was proposed that this may be due the loss of the terminal alkyl halide functionality in the PDMAEMA macro-initiator resulting from either nucleophilic cyclisation or as a result of work-up procedures. Successful gradient co-polymerisation by ATP for DMAEMA with DEAEMA was performed. The products from the gradient co-polymerisations were selectively quaternised with MeI to form a series of novel gradient co-polymer species exclusively containing quaternary charge at one end of the polymer chain.

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Chapter 6

REVERSIBLE ADDITION-FRAGMENTATION TRANSFER (RAFT) POLYMERISATION

Between the idea
and the reality
falls the shadow
T. S. Eliot

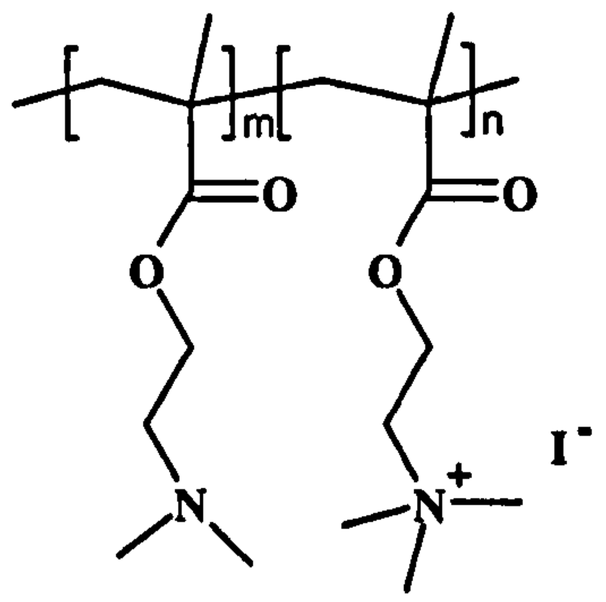
6.0 INTRODUCTION

A brief introduction to Reversible Addition-Fragmentation Transfer (RAFT) polymerisation was given in Chapter 1.5.1.3. The RAFT polymerisation system is a chain-transfer polymerisation technique that affords living polymerisation characteristics from radical polymerisation with unprecedented flexibility in the use of different monomer and solvent systems. The mechanism for the RAFT polymerisation of a vinyl monomer in the presence of a generic thiocarbonylthio transfer agent was given in Chapter 1.5.1.3.

Chong *et al* have recently reported the syntheses of narrow controlled molecular weight block co-polymers including styrene-block-dimethacrylamide, butyl acrylate-block-acrylic acid, methyl methacrylate-block-2-(dimethylamino)ethyl methacrylate) and methyl methacrylate-block-methacrylic acid [1]. These results clearly demonstrate the versatility of the RAFT process with the polymerisation of methacrylate and styrenic monomers containing basic and acidic functionality.

The use of RAFT as a possible route for the synthesis of the PDMAEMA-block PDMAEMA.MeI co-polymer (Figure 6.0) has been investigated using the current known transfer agent for methacrylate monomers.

Figure 6.0 Synthesis of PDMAEMA-block-PDMAEMA.MeI by RAFT polymerisation



This co-polymer species is of interest due to its direct analogy to the PDMAEMA-ran-PDMAEMA.MeI co-polymer. A comparison of the dye-

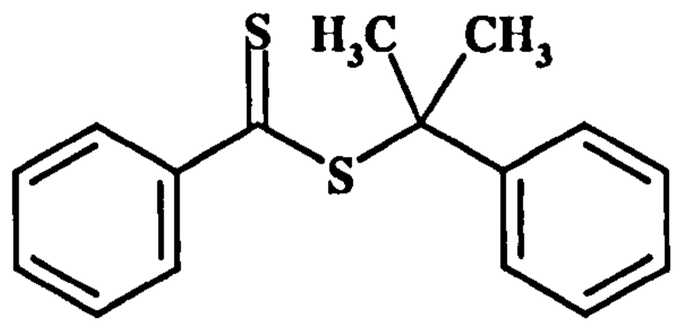
binding ability of the block co-polymer species in comparison to that of the statistical co-polymer can be used to determine whether the monomer composition can affect the dye-binding ability of the polymer species.

6.1 RESULTS AND DISCUSSION

6.1.1 Preparation of transfer agents

The synthesis of the block co-polymer PBzMA-block-PDMAEMA from RAFT polymerisation has been cited by Le *et al* where the RAFT transfer agent was 2-phenylpropy-2-yl dithiobenzoate (**6.0**). The preparation of the RAFT transfer agent 2-phenylpropy-2-yl dithiobenzoate (**6.0**) was performed following the preparation outlined by Le *et al* from dithiobenzoic acid with α-methyl styrene [2]. The product was purified by column chromatography and was obtained as a pungent smelling thick red oil.

Figure 6.1 RAFT transfer agent



2-phenylpropy-2-yl dithiobenzoate

(6.0)

The ^{1}H NMR assignment for the product agreed with that given by Le *et al* [2].

6.1.2 RAFT polymerisation of MMA with of 2-phenylpropy-2-yl dithiobenzoate transfer agent

The RAFT mediated polymerisation of MMA with 2-phenylpropy-2-yl dithiobenzoate as a transfer agent was performed following the procedure given by Le *et al* [2].

Table 6.0 gives the relative concentrations of the reagents used for the polymerisation.

Table 6.0 Reaction conditions for the RAFT polymerisation of MMA with 2-phenylpropy-2-yl dithiobenzoate (6.0) in toluene at 60° C

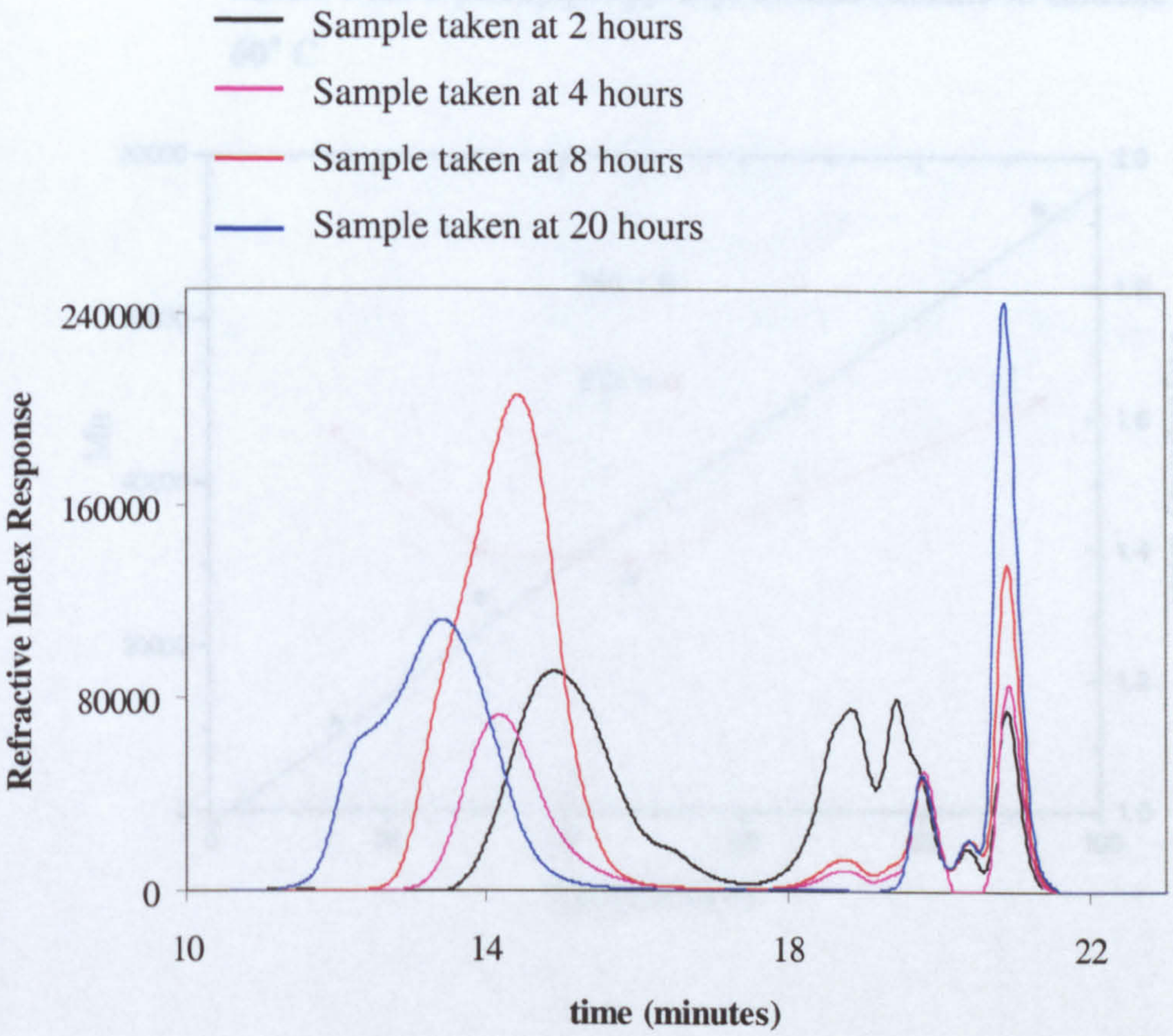
		Molar ratio		
MMA (ml)	**Toluene** (ml)	**Monomer** **[M]** MMA	**Initiator** **[I]** 2,2'-azo-bis-*iso*butyronitrile (**1.9**)	**[Transfer Agent]** 2-phenylpropy-2-yl dithiobenzoate **(6.0)**
3	1	100	0.16	0.16

Table 6.1 Molecular weight and conversion data for the RAFT polymerisation of MMA with 2-phenylpropy-2-yl dithiobenzoate (6.0) in toluene at 60° C

Sample (hours)	**Mn**	**PDi**	**Conversion** (%)	**Theoretical Mn***
2	10600	1.58	14.4	9100
4	25900	1.40	30.8	19500
8	28000	1.38	47.6	30100
20	73800	1.63	93.5	59000

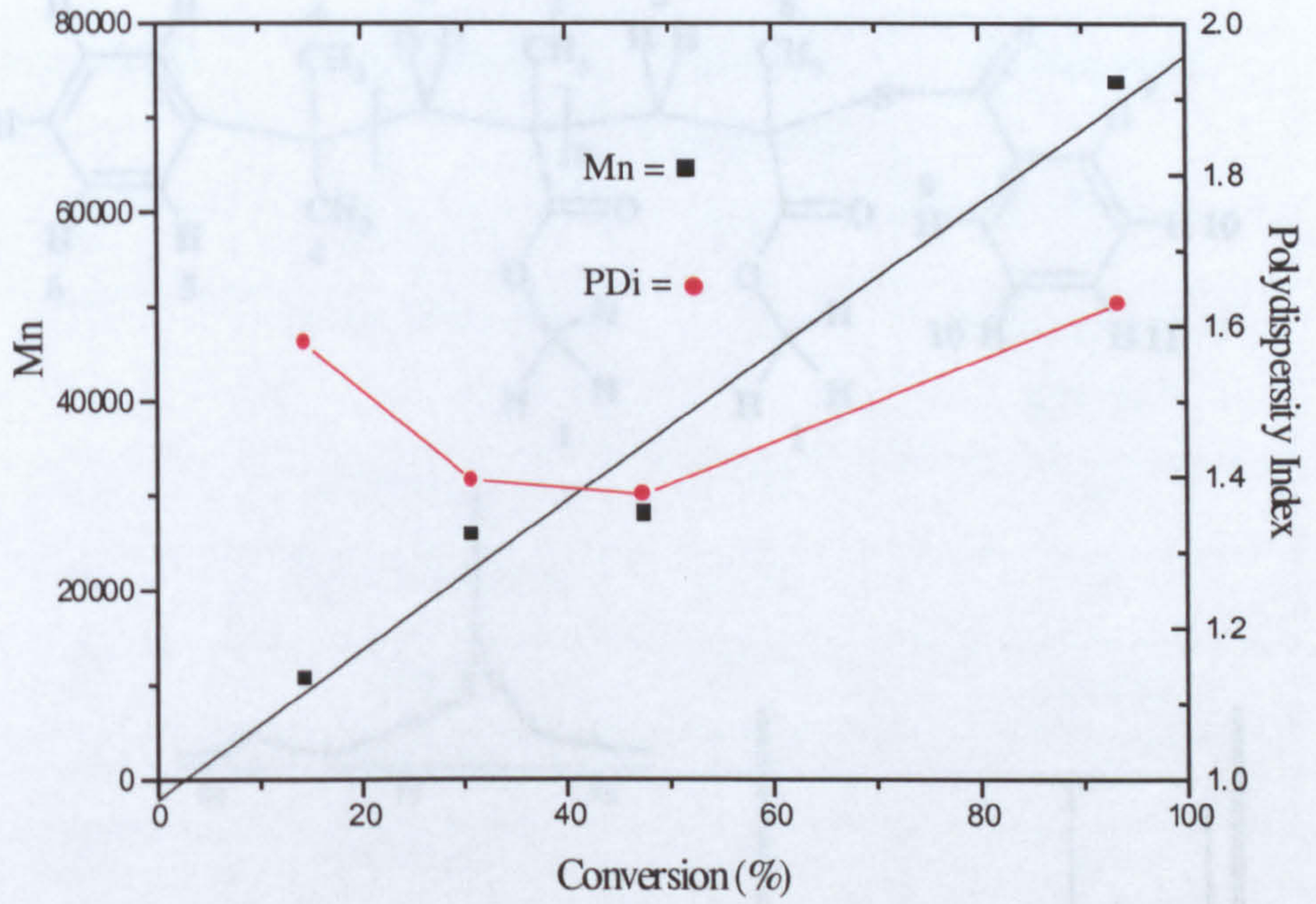
* The theoretical Mn values are calculated using equation 1.8 from Chapter 1 Section 1.5.2.

Figure 6.2 GPC spectra from the RAFT polymerisation of MMA with 2-phenylpropy-2-yl dithiobenzoate in toluene at 60 °C



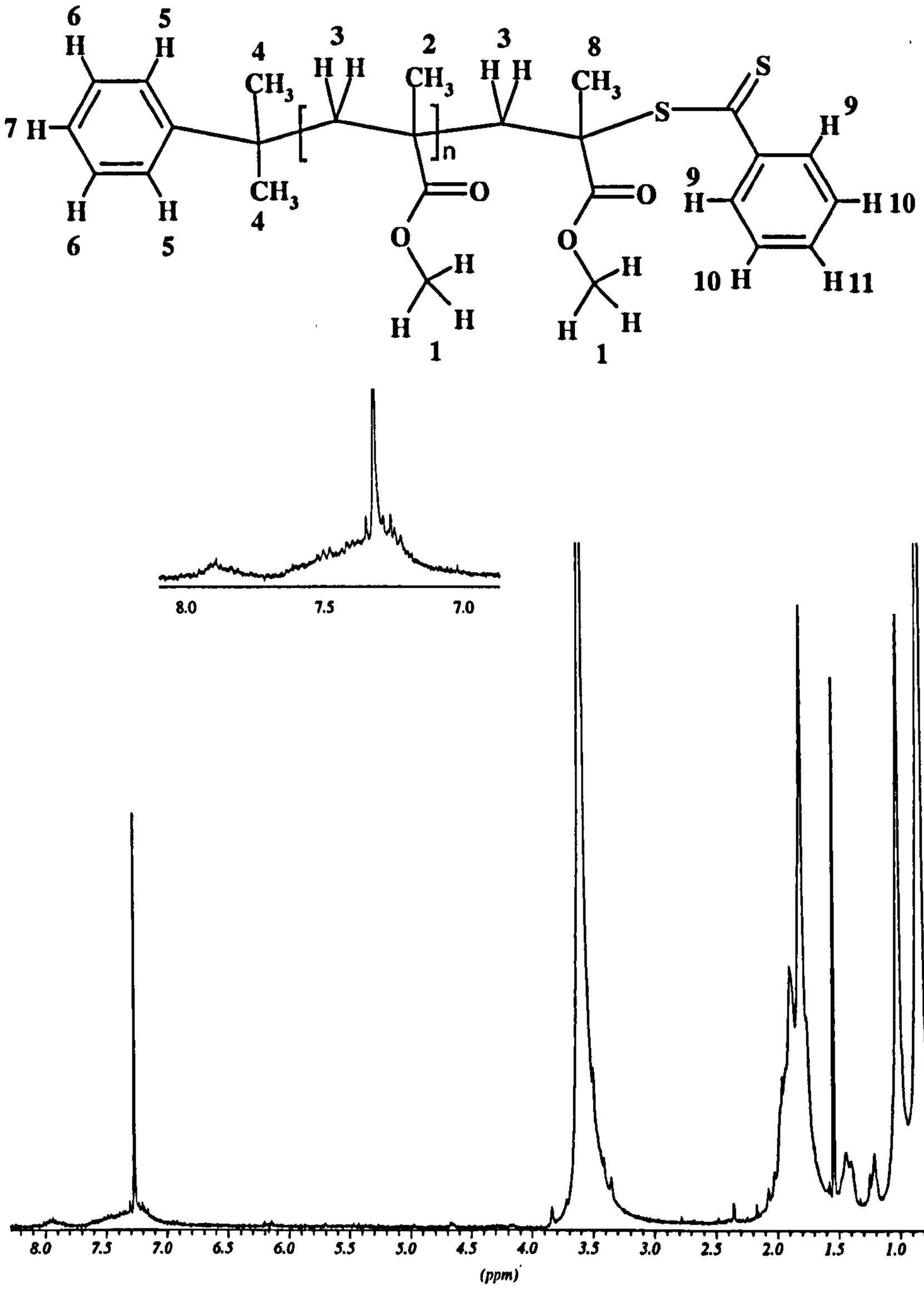
The molecular weight data and the GPC spectra show that a unimodal distribution is obtained for all samples except for the sample taken after 20 hours where a high molecular weight shoulder is present. This may be the result of termination by combination resulting from the increased termination pathways at low monomer concentrations.

Figure 6.3 **Plot of the evolution of molecular weight and polydispersity index with conversion for the RAFT polymerisation of MMA with 2-phenylpropy-2-yl dithiobenzoate in toluene at 60° C**



The ^{1}H NMR spectrum in $CDCl_3$ of the sample taken after 8 hours is given in Figure 6.4.

Figure 6.4 **250 MHz, ^{1}H NMR in $CDCl_3$ of PMMA Mn = 10600 gmol^{-1}, sample from 8 hours prepared from RAFT polymerisation with 2-phenylpropy-2-yl dithiobenzoate (6.0) transfer agent**



^{1}H NMR assignment is given in Table 6.2 based on the assignment of poly(methyl acrylate) from RAFT polymerisation given by Chiefari *et al* [3].

Table 6.2 Peak Assignment for the 250 MHz, ^1H NMR spectrum in $CDCl_3$ of the PMMA Mn = 10600 $gmol^{-1}$, prepared by RAFT polymerisation with 2-phenylpropy-2-yl dithiobenzoate (6.0) transfer agent

Chemical Shift (ppm)	Multiplicity	Relative Integration	Assignment
7.90	Multiplet	0.01	H^9
7.27	Broad Multiplet	-	$CDCl_3$, H^5,H^6, H^7, H^{10}, H^{11}
3.53	Broad Singlet	1.00	H^1
1.75	Broad Multiplet	0.57	H^2
1.52	Singlet	0.03	Impurity
1.38	Multiplet	0.03	H^8
1.26	Multiplet	0.02	H^4
0.95	Broad Multiplet	0.75	H^3

The living nature of the polymerisation system is indicated from Figure 6.3 by the linear molecular weight-conversion profile and the narrow polydispersity index of the polymerisation products. The sample taken after 20 hours displayed a larger polydispersity index than the other samples and this is explained by the increased presence of termination reactions at low monomer concentrations. This data agrees well with that given in the literature by Chiefari *et al*[3]. The ^1H NMR shows that the thiocarbonylthio functionality is incorporated into the polymer chain after termination.

6.1.3 RAFT polymerisation of DMAEMA with of 2-phenylpropy-2-yl dithiobenzoate transfer agent

The RAFT mediated polymerisation of DMAEMA with 2-phenylpropy-2-yl dithiobenzoate as a transfer agent was performed following an analogous procedure to that used for the polymerisation of MMA given in Section 6.1.2. Table 6.3 gives the relative concentrations of the reagents used for the polymerisation.

Table 6.3 **Reaction conditions for the RAFT polymerisation of DMAEMA with 2-phenylpropy-2-yl dithiobenzoate (6.0) in toluene at 60° C**

		Molar ratio		
DMAEMA (ml)	**Toluene** (ml)	**Monomer [M]** DMAEMA	**Initiator [I]** 2,2'-azo-bis-*iso*butrylnitrile **(1.9)**	**[Transfer Agent]** 2-phenylpropy-2-yl dithiobenzoate **(6.0)**
3	1	100	0.14	0.30

Table 6.4 **Molecular weight and conversion data for the RAFT polymerisation of DMAEMA with 2-phenylpropy-2-yl dithiobenzoate (6.0) in toluene at 60° C**

Sample (hours)	**Mn**	**PDi**	**Conversion** (%)	**Theoretical Mn***
4	2400	1.42	3.1	3500
8	4100	1.44	7.2	8100
20	19700	1.31	14.7	16500

* The theoretical Mn values are calculated using equation 1.8 from chapter 1 Section 1.5.2.

The molecular weight data from the GPC spectra all gave unimodal distributions.

Figure 6.5 Plot of the evolution of molecular weight and polydispersity index with conversion for the RAFT polymerisation of DMAEMA with 2-phenylpropy-2-yl dithiobenzoate in toluene at 60 °C

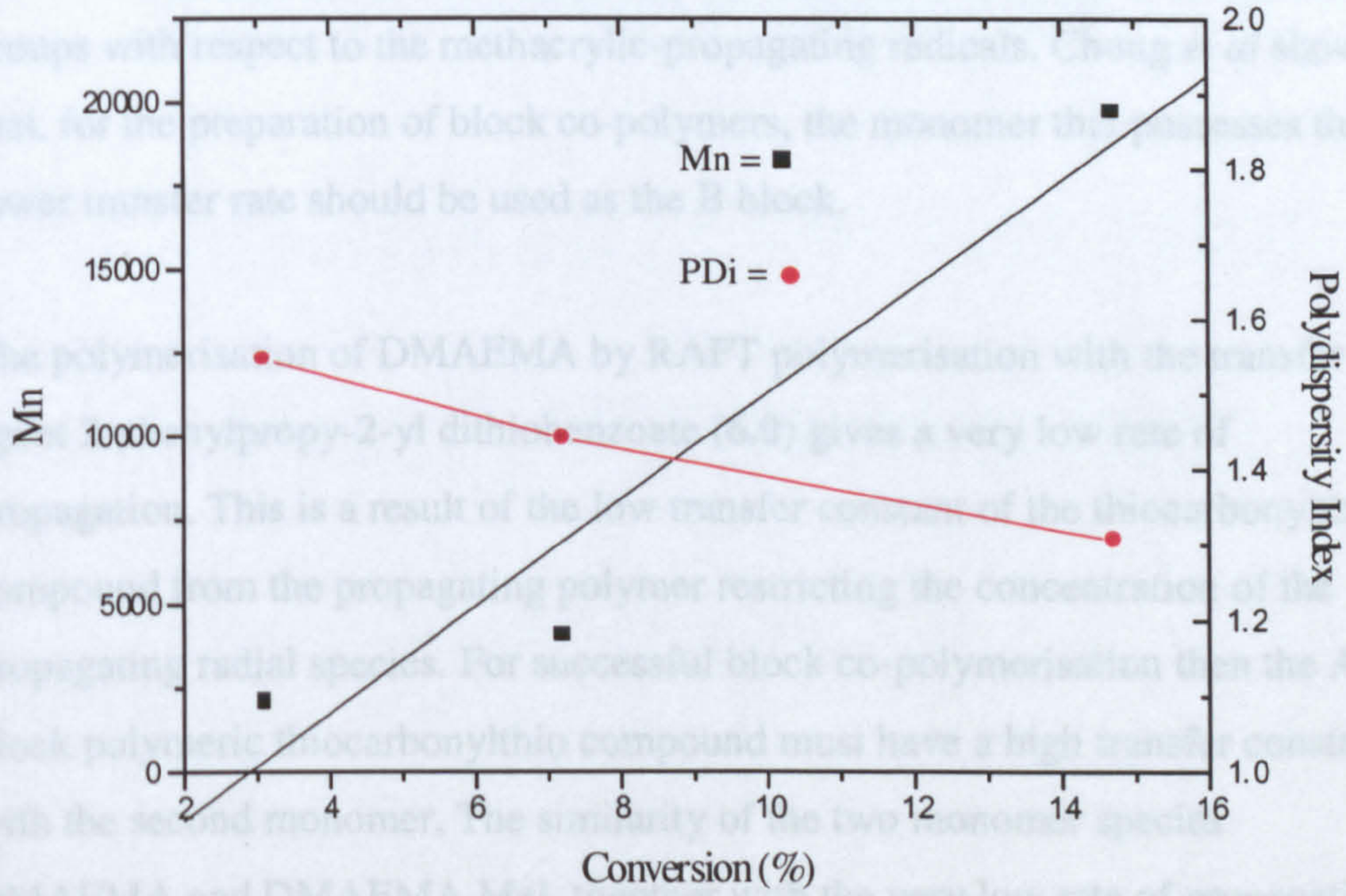


Figure 6.5 showed that molecular weight increased with respect to the instantaneous monomer conversion, suggesting that a living polymerisation system was present. The polydispersity index was reduced as the reaction proceeded. The rate of reaction for the RAFT polymerisation of DMAEMA was significantly reduced in comparison to the RAFT polymerisation of MMA when the same transfer species was used. After 20 hours of MMA polymerisation the conversion 93.5 % whereas the DMAEMA polymerisation had only reached 14.7 % monomer conversion.

6.2 CONCLUSIONS

Chong *et al* showed that a requirement for the formation of a narrow polydispersity AB block co-polymers in a batch RAFT polymerisation is that the initially formed A-block polymeric thiocarbonylthio compound should have a high transfer constant in the subsequent polymerisation step to give the B block [1]. When the A-block is a poly(acrylate ester) or polystyrene chain the transfer constants in methacrylate polymerisation appear to be very low. This was attributed to the styrenic or acrylic propagating radicals being poor leaving groups with respect to the methacrylic-propagating radicals. Chong *et al* showed that, for the preparation of block co-polymers, the monomer that possesses the lower transfer rate should be used as the B block.

The polymerisation of DMAEMA by RAFT polymerisation with the transfer agent 2-phenylpropy-2-yl dithiobenzoate (**6.0**) gives a very low rate of propagation. This is a result of the low transfer constant of the thiocarbonylthio compound from the propagating polymer restricting the concentration of the propagating radial species. For successful block co-polymerisation then the A-block polymeric thiocarbonylthio compound must have a high transfer constant with the second monomer. The similarity of the two monomer species DMAEMA and DMAEMA.MeI, together with the very low rate of propagation of the initial DMAEMA polymerisation means that controlled block co-polymerisation using RAFT polymerisation is difficult to perform. The emerging nature of the RAFT polymerisation technology and the high toxicity and odour of the transfer agents meant that no further RAFT polymerisation was performed. Moad *et al* have recently published papers showing that block co-polymer preparation with RAFT mediated polymerisation is possible for DMAEMA [1,4]. However all cited examples had DMAEMA as the second B block following the successful synthesis of an polyacrylate thiocarbonylthio compound

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Chapter 7

DETERMINATION OF THE DYE-BINDING ABILITY OF SYNTHETIC POLYMERS

Kierkegaard Søren

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forwards lived be must Life

7.0 INTRODUCTION

A range of different tests have been developed and performed to determine the degree of dye-transfer that occurs in the presence of different water-soluble polymers synthesised during this research project. A series of qualitative tests based on simulated laundering cycles were performed to screen the initial materials that were synthesised. A series of laboratory tests were then developed and used to determine a value for the dye-binding constant, K_P, of selected polymers.

7.1 QUALITATIVE MEASUREMENT OF THE DYE-BINDING ABILITY OF WATER SOLUBLE POLYMERS

A variety of different test procedures based on simulated laundering cycles were developed to determine the degree of dye-transfer that occurred in the presence of water-soluble polymers. These tests were performed during several visits to the Fabric Care Unit at Unilever Central Research, Port Sunlight (UK). These tests were used to screen initial polymer products to assess their potential as anti-dye transfer agents.

7.1.1 Tests to determine the degree of dye-transfer that occurs from a dyed cotton cloth onto a white non-bleached cotton cloth under simulated laundering conditions

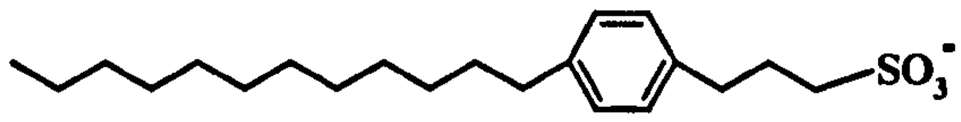
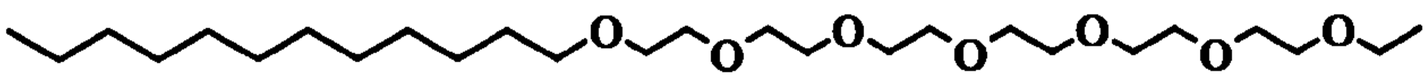
A test was developed that would determine how much dye-transfer occurred during a simulated laundering cycle between a pre-dyed cotton cloth and a cotton cloth that had not been dyed or bleached. Tests were performed on polymers from present commercial formulations and on a range of different possible anti-dye transfer agents prepared from radical polymerisation and catalytic chain transfer mediated polymerisation. Reflectance UV-visible

spectrometry was used to measure the relative concentration of dye present on all of the cotton cloths used in the experiments both before and after laundering.

All simulated laundering tests were performed using a 'tergometer'. A tergometer comprises a steel beaker that is suspended into a temperature controlled water bath. A wash formulation can then be added to the steel container and the mixture is then stirred from above using an over head stirrer designed to simulate a top loading American style washing machine. The stirring method uses a repeated cycle of one clockwise revolution of 180 degrees followed by an anti-clockwise revolution of 180 degrees. For each experiment the temperature of the water bath and the speed of stirring can be adjusted as desired.

Each test was performed using a mixture of detergent stock, polymer stock solution and demineralised water. The formulation for the stock solution used is given in Figure 7.0. This formulation is based on the principal active ingredients that are present in Persil 'colour' non-biological soap detergent. No fragrance is added and the active 'colour' ingredient is omitted. This allows comparison of new synthetic anti-dye transfer agents with those already used in the commercial Persil 'colour' formulations.

Figure 7.0 Surfactant stock formulation

Chemical	Activity	Concentration
Linear Alkyl Sulphonate (LAS) **(7.0)**  Supplier, Petrelab 550. Average C_{12} chain, not always linear	Anionic Surfactant	1.6 gl^{-1}
Ethoxylated nonionic A7 (A7) **(7.1)**  Supplier, Synperionic A7. Average $C_{12}H_{25}$ $C_{14}H_{29}O_7$ chain	Nonionic Surfactant	0.4 gl^{-1}
Sodium Tripolyphosphate (STP) **(7.2)** $Na_5P_3O_{10}$	Anti-redeposition agent and metal extraction active	1.2 gl^{-1}
Sodium Carbonate **(7.3)** Na_2CO_3	To increase ionic strength and pH	0.4 gl^{-1}

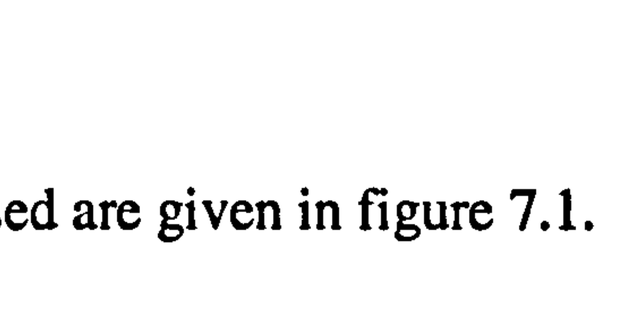
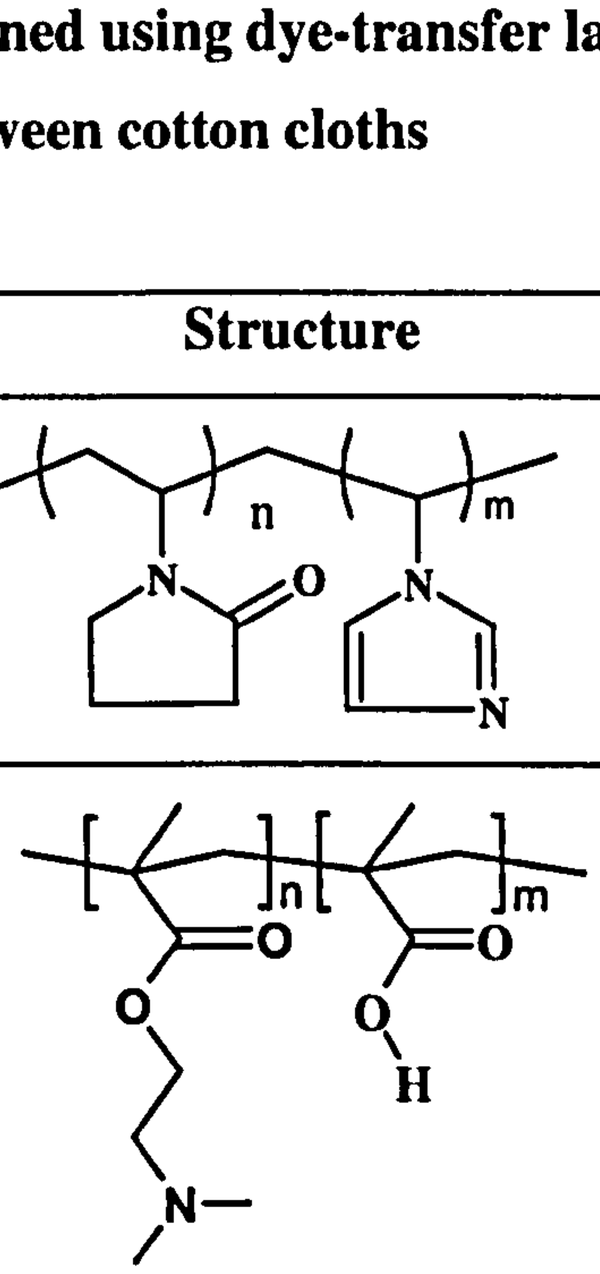
A polymer stock solution was prepared using demineralised water to give an effective concentration based on 1.7 % by weight added with respect to cloth. Two pink cotton cloths, pre-dyed with Direct Red 80 azo dye (**1.1**) of 10 cm^2 and one non-dyed cotton cloth of 13 cm^2 were used for each experiment. No fixative was added to the pre-dyed cotton cloths.

For each test 450 ml of demineralised water was added to the stainless steel beaker. 25 ml of surfactant stock was added and the solution was warmed to 40 °C. Polymer stock (25 ml) was added and the resulting solution was allowed to equilibrate for ten minutes. The cotton cloths were added to the beaker and then the mixture was maintained at 40 °C and was stirred at 70 rpm for 30 minutes. After washing the cloths were removed and aired to evaporate all water. After the initial washing cycle the cloths were dried and analysed for dye-transfer.

Two more wash and dry cycles were then performed where no further polymer added. This allows the rate of dye-transfer for a multi-wash regime to be determined and also gives an indication of the ability of the polymer to bind at the cotton surface and remain active for repeated washes. The delta reflectance at 534 nm (λ max for direct red 80) was measured for each cotton cloth before and after each washing and drying cycle. This gives relative data concerning the amount of dye that is present on the cloth surface. A plot of dye loss from the dyed cotton cloths and dye pick up onto the white cloth are given for a series of different polymers.

The polymers that were analysed are given in figure 7.1.

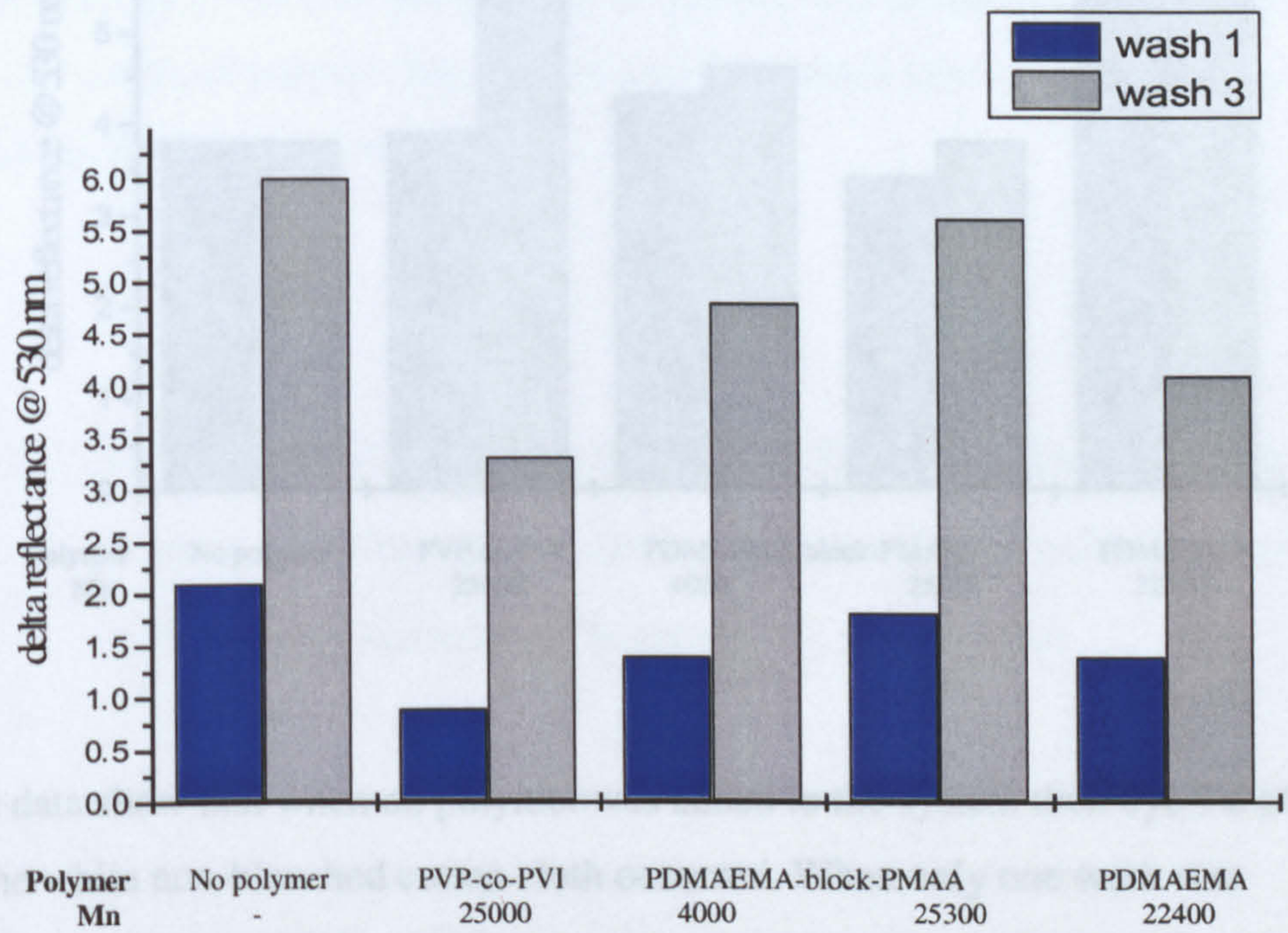
Figure 7.1 Polymers screened using dye-transfer laundering simulation between cotton cloths

Polymer	Structure	Mn
PVP-co-PVI (7.4) (industrial statistical co-polymer)		25000
PDMAEMA-block-PMAA (a)		4000 (a)
PDMAEMA-block-PMAA (b)		25300 (b)
PDMAEMA (2.1)		22400

This initial screen was designed to examine the potential of PDMAEMA and its block co-polymer species as anti-dye transfer agents.

Figure 7.2 illustrates the degree of dye loss determined for each polymer after 1 wash and after 3 successive washes. The degree of dye loss is quoted, as 'delta reflectance' which is the value of the amount of dye lost from the cotton cloth with respect to the original cloth before the first wash cycle.

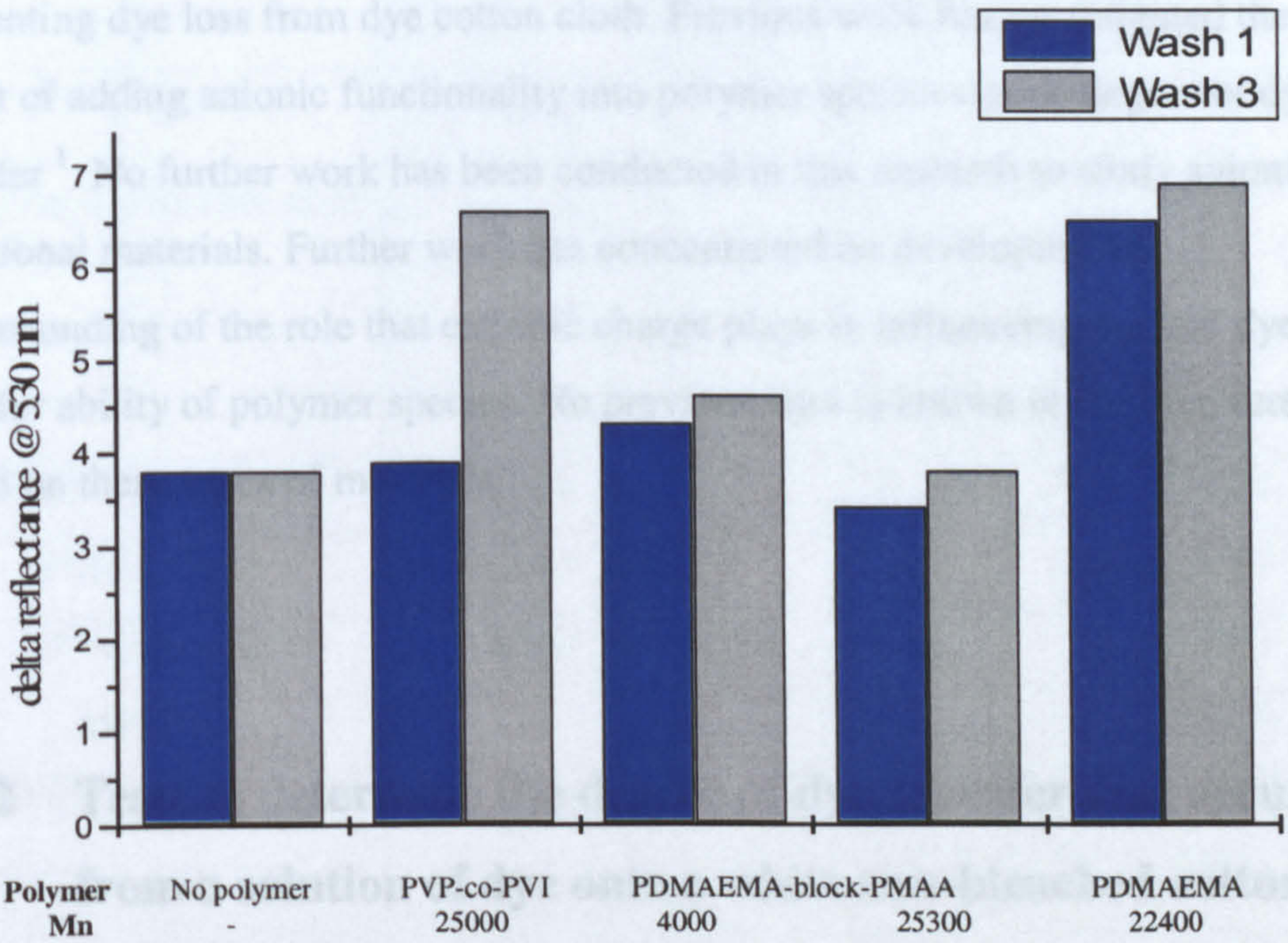
Figure 7.2 Effect of polymer on loss of dye from a dyed cotton cloth



The data show that all polymers reduce the amount of dye loss from the fabric in comparison to the control study where no polymer is added. The conventional anti-dye transfer agent PVP-co-PVI retained the most dye in the cloth and the homopolymer of PDMAEMA performed second best. The addition of anionic functionality from methacrylic acid reduced the effectiveness of the polymer at preventing dye transfer. This is presumably due to electrostatic repulsion between the anionic dye and the anionic methacrylic acid functionality. These results mimic those reported in the literature where acrylic acid is incorporated into a statistical co-polymer with N-vinyl pyrrolidone [1]. These initial results

show that the incorporation of cationic polymers into the laundering cycle can reduce the degree of dye loss from the dyed cotton cloth.

Figure 7.3 Effect of polymer on the pick up of dye onto white non-dyed cotton cloth from a dyed cotton cloth



The data show that when no polymer was added to the system then dye transfer to the white non-bleached cotton cloth occurred. When only one wash was performed then the PVP-co-PVI polymer and the block co-polymers of PDMAEMA with MAA give similar data to that obtained from the control experiment, where no polymer was added. When the PDMAEMA and PVP-co-PVI were added over a three wash cycle then more dye was transferred to the cloth than that transferred without any polymer being present. The data show that the addition of the PDMAEMA homopolymer to the laundering cycle results in an increase in the degree of dye-transfer to the non-bleached cotton cloth. This is presumed to be the result of hydrogen bond formation between the cationic polymer and the cellulose fibre of the cotton cloth. As a degree of anionic functionality is incorporated into the polymer then the amount of dye transfer to the white non-bleached cotton cloth is reduced.

These results show that the addition of cationic polymers to the laundering cycle is a balance between the beneficial reduction in the degree of dye loss from the dyed cotton cloth and the undesirable increase in dye pick up at the white non-bleached cotton cloth. The addition of anionic functionality into the polymeric species has been shown to decrease the effectiveness of the polymer in preventing dye loss from dye cotton cloth. Previous work has investigated the effect of adding anionic functionality into polymer species on the degree of dye-transfer [1]. No further work has been conducted in this research to study anionic functional materials. Further work has concentrated on developing an understanding of the role that cationic charge plays in influencing the anti dye-transfer ability of polymer species. No previous data is known in the literature based on these types of materials.

7.1.2 Tests to determine the degree of dye-transfer that occurs from a solution of dye onto a white non-bleached cotton cloth under simulated laundering conditions

A new series of tests were performed to determine the degree of dye pick up that occurred onto a white non-bleached cotton cloth from a wash solution containing surfactant stock, dye and the test polymer. For each test a 10 μM solution of Direct Red 80 dye was prepared into 100 ml of demineralised water containing 5 ml of surfactant stock solution (Figure 7.0). A white non-bleached cotton cloth (13 cm^2) and the test polymer (0.0435 gl^{-1}) were then added and the mixture was agitated in a tergometer for 30 minutes at 40 °C.

The different polymers that were analysed using this method are given in Table 7.0.

Table 7.0 Polymers analysed for the pick-up of dye from solution onto a white non-bleached cotton cloth

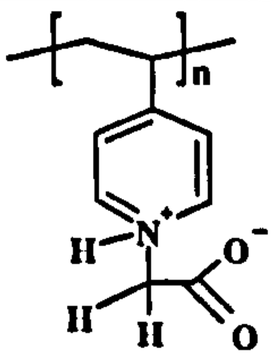
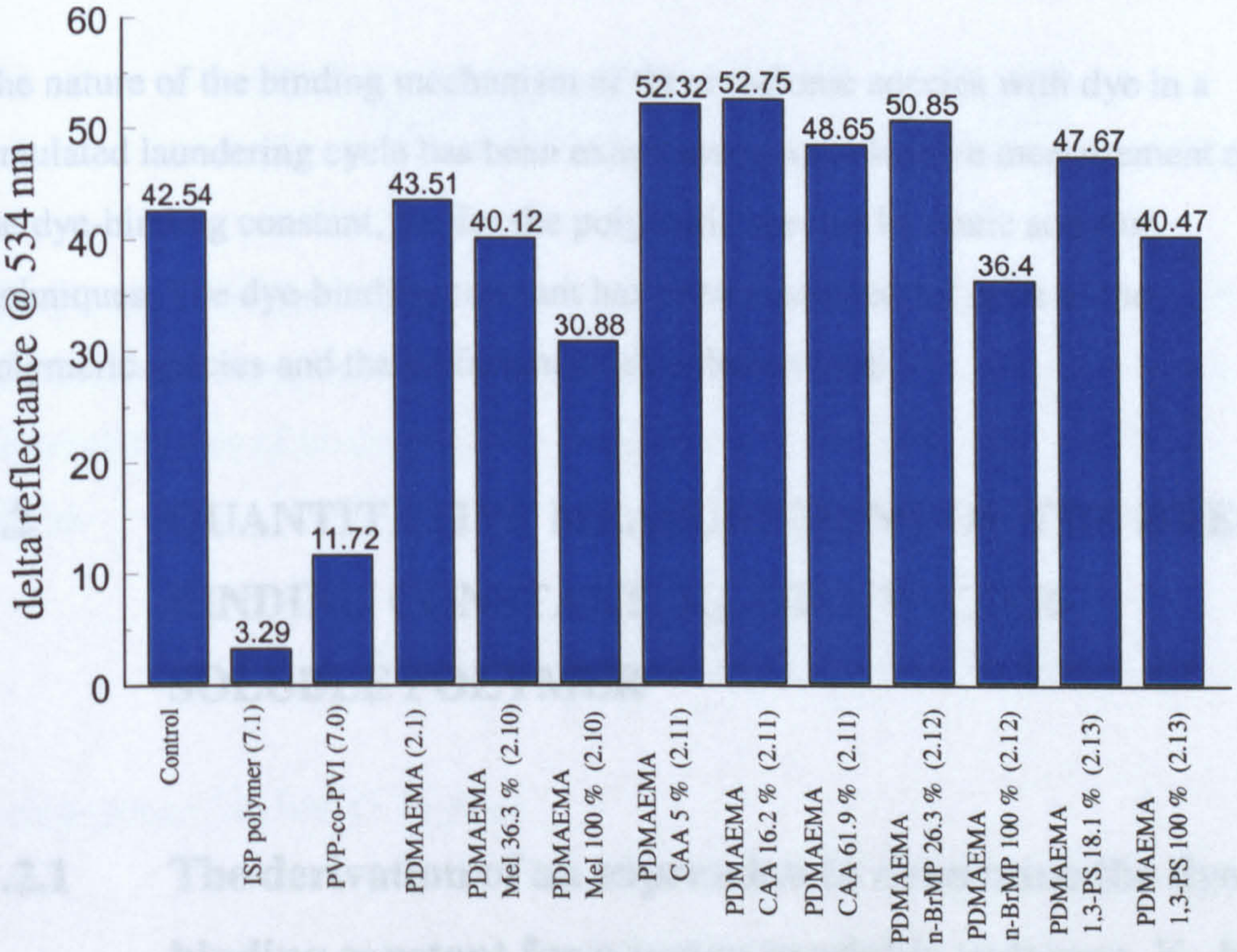
Polymer	Structure	% quaternisation with respect to DMAEMA	Mn
ISP polymer, Polyvinyl pyridinic acid	 **(7.5)**	0	25000
PVP-co-PVI	**(7.4)**	0	25000
PDMAEMA	**(2.1)**	0	22400
PDMAEMA. MeI salt	**(2.10)**	36.3	30000
		~100	42400
PDMAEMA. Chloroacetic acid (CAA) salt	**(2.11)**	5	23100
		16.2	25000
		61.9	27600
PDMAEMA. n-bromomethyl phthalimide (n-BrMP) salt	**(2.12)**	26.3	31300
		~100	56400
PDMAEMA. 1,3-propane sultone (1,3-PS) salt	**(2.13)**	18.1	25400
		~100	39600

Figure 7.4 shows the data corresponding to dye pick up by the white cotton cloths after washing and drying.

Figure 7.4 Effect of polymer on the pick up of dye from solution onto a white non-dyed cotton cloth



The ISP polymer and the PVP-co-PVI polymer both gave a large reduction in the degree of dye pick-up onto the white non bleached cotton cloth compared with the control test, where no polymer was added. The addition of the PDMAEMA homopolymer and its derivatives showed little or no reduction in the degree of dye transfer in comparison to the control test.

The results from these preliminary qualitative tests to determine the degree of anti-dye transfer activity of polymer species in simulated laundering cycles has shown that the nature of dye-transfer in a simulated wash is a complex process that can be influenced by polymer species. It has been shown that the addition of a cationic polymeric species to the laundering cycle can effectively reduce the degree of dye loss from the dyed cotton cloth. It has also been shown that the addition of cationic species into the laundering cycle, where free dye is present in solution can reduce the degree of dye pick-up onto the cotton cloth. The incorporation of permanent cationic charge into the polymer species reduced the degree of dye pick-up onto the cotton cloth. The nature of the permanent cationic charge was shown to influence the degree of dye transfer.

The addition of methyl iodide to form the quaternary ammonium salt gave the largest reduction in the degree of dye pick-up onto the cotton cloth.

The nature of the binding mechanism of these cationic species with dye in a simulated laundering cycle has been examined by quantitative measurement of the dye-binding constant, K_P, for the polymeric species by static sorption techniques. The dye-binding constant has been evaluated for each of the polymeric species and the surfactant stock solution used.

7.2 QUANTITATIVE MEASUREMENT OF THE DYE-BINDING CONSTANT, K_P, OF A WATER-SOLUBLE POLYMER

7.2.1 The derivation of an expression to determine the dye-binding constant for a water-insoluble polymer, K_S by static sorption

To determine the dye-binding equilibrium constant, K_P, for a water-soluble polymer by static sorption it was shown in Chapter 1 section 1.2.1.2 that it is first necessary to determine the dye-binding equilibrium constant for a water-insoluble cross-linked (CL) polymer, K_S. The value of K_S for the cross-linked polymer is required to calibrate the data obtained from the dye–binding study with a water-soluble polymer.

The equations that are needed to determine the dye-binding constant for an insoluble polymer with a dye are derived here [2-7].

K_S is the binding constant for a cross-linked polymer in the solid phase. K_S is defined as the ratio of the total occupied binding sites $[CL.D]_S$ with respect to the product of the free binding site concentration for the cross-linked polymer $[CL]_S$ and the dye concentration in the liquid phase $[D]_L$. Subscript '$_S$' refers to

components in the solid phase and subscript '$_L$' refers to components in the liquid phase.

$$K_S = \frac{[CL.D]_S}{[D]_L[CL]_S} \qquad (7.1)$$

$[CL]_S$ is the total free binding site concentration for the polymer and is equal to the number of occupied binding sites at equilibrium $[CL.D]_S$ subtracted from the total number of binding sites in the polymer before the addition of dye $[CL_0]_S$

$$[CL]_S = [CL_0]_S - [CL.D]_S \qquad (7.2)$$

Substituting (7.2) into (7.1) gives:

$$K_S = \frac{[CL.D]_S}{[D]_L([CL_0]_S - [CL.D]_S)} \qquad (7.3)$$

Consider the mass distribution of the dye in the system, dye is initially equilibrated between the free dye and the dye in the solid polymer compartment.

$$D_O = D_L + D_S \qquad (7.4)$$

The phase ratio φ, is introduced.

$$\varphi = \frac{V_S}{V_L} \qquad (7.5)$$

V_S is the volume in the polymer phase and V_L is the volume in the liquid phase. The total mass of dye in the system, D_0 is equilibrated according to equation (7.4), dividing throughout by the volume in the system gives the relative concentration distribution.

$$\frac{D_0}{V_L} = \frac{D_L}{V_L} + \frac{D_S}{V_L} \qquad (7.6)$$

$$[D_O]_L = [D]_L + \left(\frac{V_S[D]_S}{V_L}\right)_S \qquad (7.7)$$

The concentration of dye in the solid polymer compartment is equilibrated between dye in the bound state and dye in the free state that is trapped in the free volume, where both must be treated separately from the free dye in the liquid compartment.

$$[D]_S = [D]_L + [CL.D]_S \qquad (7.8)$$

Substitution of (7.8) into (7.7) gives:

$$[D_O]_L = [D]_L + \left(\frac{V_S[D]_L}{V_L} + \frac{V_S[CL.D]_S}{V_L}\right)_S \qquad (7.9)$$

Substitution of the phase ratio, equation (7.5) into (7.9) gives:

$$[D_O]_L = [D]_L + \varphi([D]_L)_S + \varphi[CL.D]_S \qquad (7.10)$$

Rearranging (7.10) in terms of $[CL.D]_S + ([D]_L)_S$ gives:

$$[CL.D]_S + ([D]_L)_S = \frac{1}{\varphi}([D_O]_L - [D]_L) \qquad (7.11)$$

For systems containing low concentrations of dye ($[D]_0 < 1 \times 10^{-6}$ M) it can be assumed that the fraction of dye in the polymer phase that does not bind with polymer and is present in the free volume is negligible in comparison with the total concentration of dye in the liquid phase, i.e., $([D]_L)_S = 0$; this is the assumption that is made in the literature data [7]. In real terms the proportion of the dye in the solid polymer phase for cross-linked PVP-CL that is present as

the bound species $[CL.D]_S$ is 88.6 % of the total dye in the solid polymer phase. This is supported by data given in section 7.2.2.4. Equation 7.11 becomes:

$$[CL.D]_S = 0.886\left(\frac{1}{\varphi}([D_O]_L - [D]_L)\right) \qquad (7.12)$$

Equation 7.12 allows the determination of the concentration of bound sites $[CL.D]_S$ from experimental data. The value of $[CL.D]_S$ can then be substituted into equation 7.3 to allow the experimental determination of the dye-binding constant for a water-insoluble polymer, K_S.

7.2.2 Determination of the dye-binding constant for a cross-linked poly(N-vinyl pyrrolidone) water-insoluble polymer, K_S from static sorption

The validity of an experimental procedure for determining K_S by static sorption is dependent on several factors:

1) The absolute concentration of free dye that is present in the stock solution must be known.
2) No aggregation of dye must occur during the testing process.
3) The minimum length of time for dye-binding equilibrium to be established must be known.
4) The stability of the polymer-dye adduct $[CL.D]_S$ must be determined.

A series of experiments were performed to determine these factors.

7.2.2.1 Measurement of the dye content in industrial Direct Red 80 dye

Direct Red 80 dye was purchased from the Aldrich Chemical Co. Almost all industrially available azo-dyes including Direct Red 80 are supplied as a powder

containing a large degree of impurity, these are typically inorganic salts. Elemental analysis of the dye as supplied by Aldrich Chemical Co was used to determine the actual dye content based on the theoretical percentage of carbon present.

The theoretical carbon content for pure Direct Red 80 is 39.36%, the actual carbon content that was found for the Direct Red 80 as supplied from Aldrich Chemcial Co was 11.90%.

$$(11.90/39.36)x100 = 30.23\ \%$$

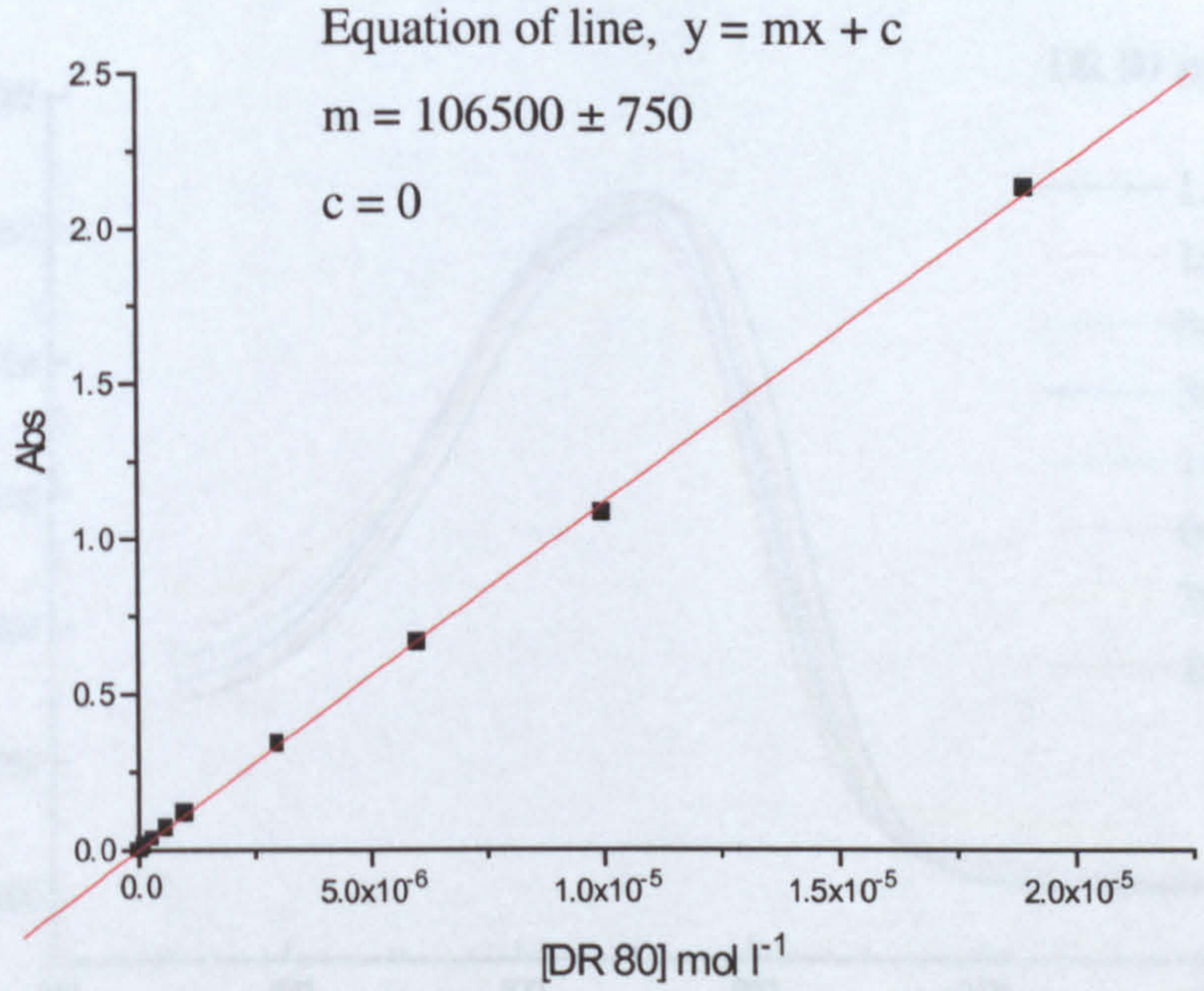
A series of dye stock solutions was prepared based on the value of dye content from the elemental analysis data. Table 7.1 lists the composition of the dye stock solutions in 1 litre of distilled water.

Table 7.1 Direct Red 80 dye stock solution composition

DR 80 powder (g)	Content of DR 80 dye based on 30.23% purity (g)	Concentration Mol l^{-1}
$4.5x10^{-4}$	$1.4x10^{-4}$	$1x10^{-7}$
$1.4x10^{-3}$	$4.1x10^{-4}$	$3x10^{-7}$
$2.7x10^{-3}$	$8.2x10^{-4}$	$6x10^{-7}$
$4.5x10^{-3}$	$1.4x10^{-3}$	$1x10^{-6}$
$1.4x10^{-2}$	$4.1x10^{-3}$	$3x10^{-6}$
$2.7x10^{-2}$	$8.2x10^{-3}$	$6x10^{-6}$
$4.5x10^{-2}$	$1.4x10^{-2}$	$1x10^{-5}$
$8.6x10^{-2}$	$2.6x10^{-2}$	$1.9x10^{-5}$

Each stock solution was accurately prepared by the dilution of an initial stock solution prepared at $5x10^{-5}$ mol l^{-1}. The UV/Visible spectra of these dye solutions were performed and the λ-max at 534 nm was obtained.

Figure 7.5 Beer-Lambert plot for Direct Red 80 dye in aqueous solution at 534 nm



The gradient, m is equal to the extinction coefficient for Direct Red 80.

$$A = ECL \qquad (7.13)$$

A is the Absorbance, E is the extinction coefficient, C is the concentration and L is the path length of 1 cm.

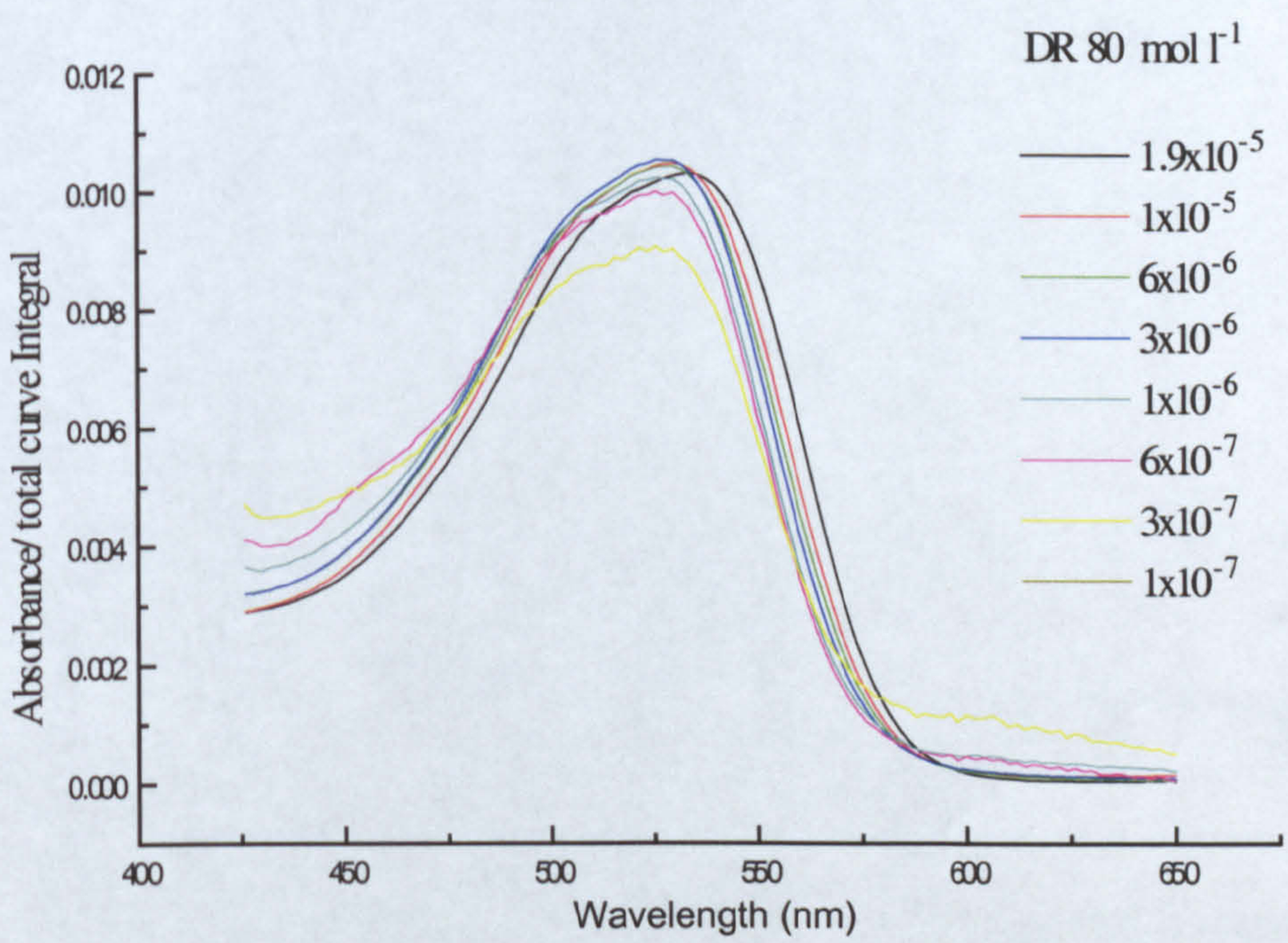
The concentration of all unknown Direct Red 80 solutions is calculated using the determined value for the extinction coefficient, E = 106500 ± 750.

7.2.2.2 The determination of the aggregation behaviour for Direct Red 80 dye

It is necessary to verify that Direct Red 80 does not aggregate in solutions over the range of concentrations for which the tests will be performed. Aggregation

of dye is accompanied with a bathochromic shift for the λ-max of the absorption spectrum. The spectra obtained for each of the dye solutions was integrated for each data point and normalised; the overlaid spectra are given in Figure 7.6.

Figure 7.6 Normalised plot of Absorbance versus Wavenumber for stock Direct Red 80 dye solutions



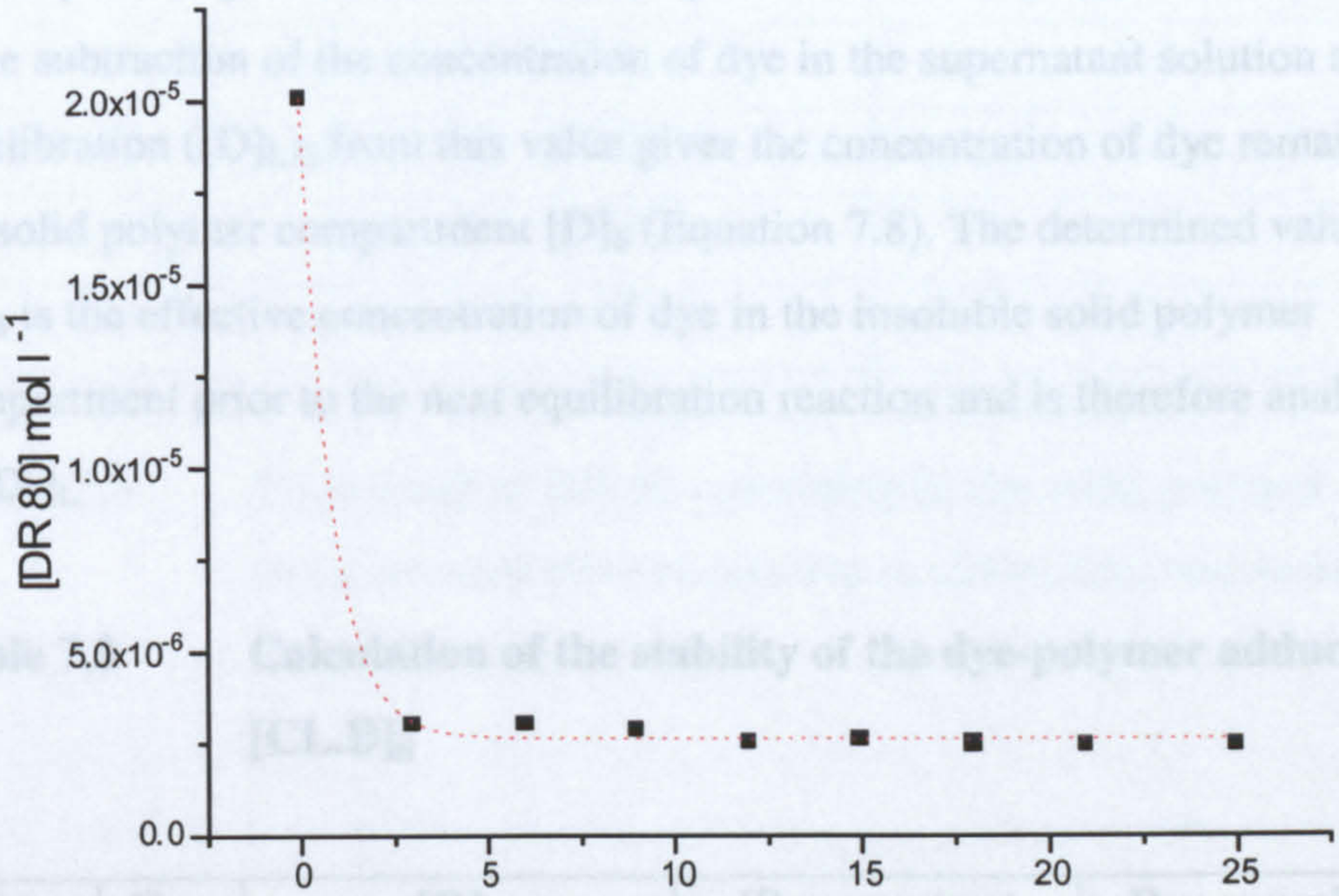
The overlay of spectra for the stock solutions containing Direct Red 80 shows that no measurable shift in the λ-max occurs over the concentration range examined. No aggregation of the dye has occurred and therefore Direct Red 80 is a suitable dye for the determination of the binding constant by static sorption.

7.2.2.3 Measurement of the time required for dye-binding equilibration to occur between cross-linked poly(N-vinyl pyrrolidone) and Direct Red 80 dye

A dye stock solution (~1.9 x 10^{-5} M) was prepared and divided into 50 ml aliquots. To each, 0.5 g (10 g l^{-1}) of cross-linked poly(N-vinyl pyrrolidone) was added. Each mixture was shaken for a specific length of time before removal and separation by centrifugation at 5000 rpm for 15 minutes. The concentration

of the supernatant solution was determined by UV/Visible spectrometry and from this the concentration of dye remaining in solution was determined.

Figure 7.7 Concentration of DR 80 remaining in solution after mixing with cross-linked poly(N-vinyl pyrrolidone)



The data show that the dye-binding equilibrium is governed by an exponential decay of dye concentration. Equilibrium is completely reached after 18 minutes of shaking. It was decided that for all subsequent tests that 25 minutes would be allowed for equilibrium to be established.

7.2.2.4 Measurement of the stability of the polymer-dye adduct $[CL.D]_S$

An experiment to determine the stability of the polymer-dye adduct $[CL.D]_S$ and the degree of dye present in the free volume in the solid polymer compartment $([D]_L)_S$ was performed. A stock solution of Direct Red 80 (~1.9 x 10^{-5} M) was prepared. A 50 ml aliquot was mixed with 0.5 g (10 g l^{-1}) cross-linked poly(N-vinyl pyrrolidone). The mixture was agitated for 25 minutes and then the cross-linked polymer-dye adduct was isolated by centrifugation (5000

rpm for 60 minutes). The visible spectra of the supernatant solution was determined and then the isolated polymer-dye adduct was added to 50 ml of deionisd water and shaken for 25 minutes and then isolated. This process was repeated 3 more times to establish how much dye was lost from the polymer-dye adduct during each repetition. Table 7.1 outlines the calculation of data for each repetition performed. The initial dye concentration $[D_0]_L$ is $1.99x10^{-5}$ mol.l^{-1}, the subtraction of the concentration of dye in the supernatant solution after equilibration $([D]_L)_S$ from this value gives the concentration of dye remaining in the solid polymer compartment $[D]_S$ (Equation 7.8). The determined value of $[D]_S$ is the effective concentration of dye in the insoluble solid polymer compartment prior to the next equilibration reaction and is therefore analogous to $[D_0]_L$.

Table 7.2 Calculation of the stability of the dye-polymer adduct $[CL.D]_S$

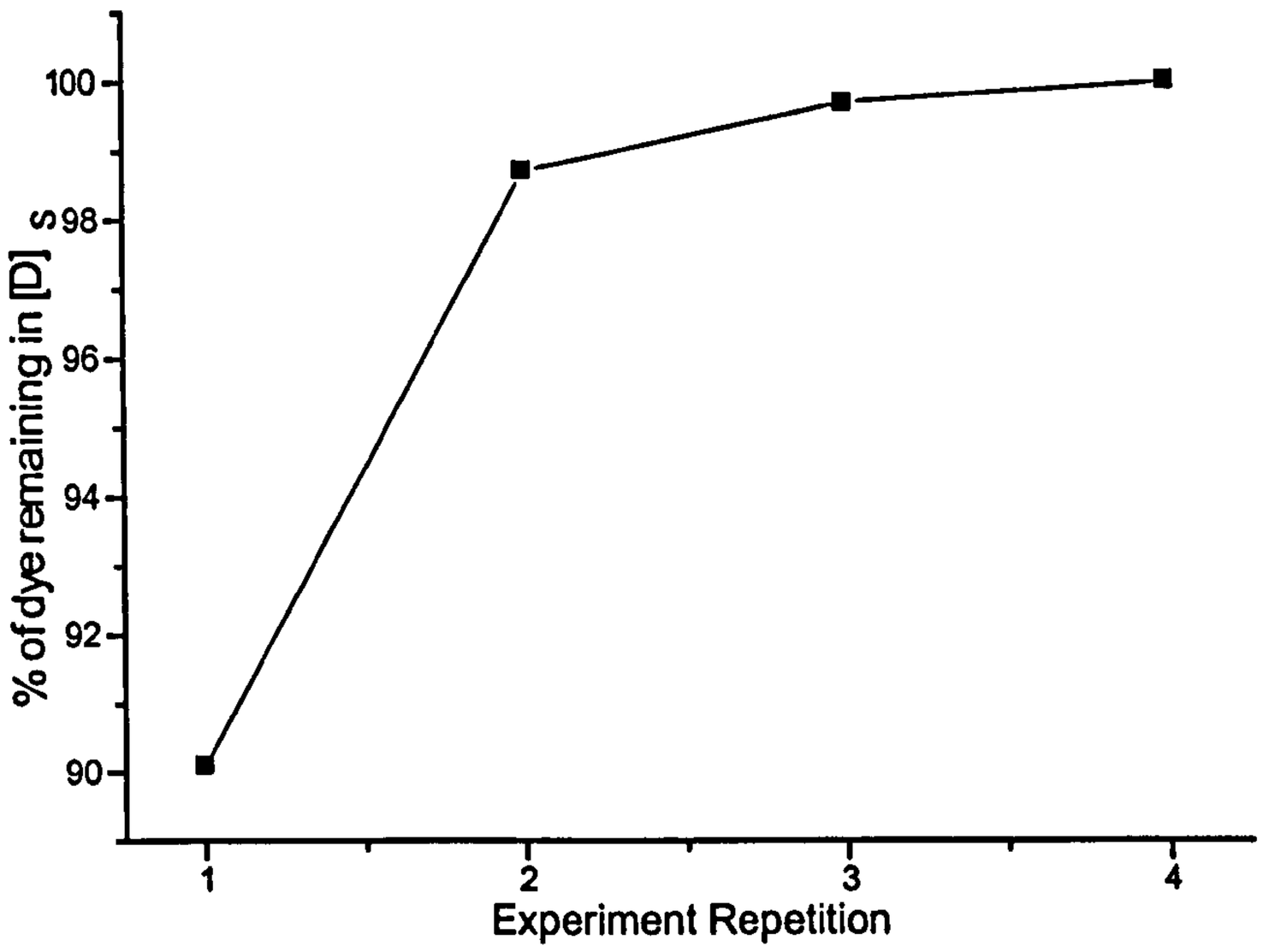
Time (mins)	Exp	$[D]_S$ (Mol)	[Supernatant dye solution], $([D]_L)_S$	Dye remaining in solid polymer compartment
0	0	-	-	$1.81x10^{-5}$
25	1	$1.81x10^{-5}$	$1.80x10^{-6}$	$1.63x10^{-5}$
50	2	$1.63x10^{-5}$	$2.08x10^{-7}$	$1.61x10^{-5}$
75	3	$1.61x10^{-5}$	$4.71x10^{-8}$	$1.61x10^{-5}$
100	4	$1.61x10^{-5}$	~0	$1.61x10^{-5}$

A plot of the percentages of dye remaining in the solid polymer compartment after equilibration as a fraction of $[D]_S$ shows how the loss of dye from the solid polymer compartment varies with repeated experiments.

Table 7.3 Data for percentages of dye remaining and lost from the solid polymer compartment with repeated experiments

Experiment	Dye remaining in solid polymer compartment (%)	Dye lost into supernatant solution (%)
1	90.1	9.9
2	98.7	1.3
3	99.7	0.3
4	100	0

Figure 7.8 Percentage of DR 80 remaining in the solid polymer compartment after successive equilibration and isolation in deionised water



After four repetitions a state is reached where no further dye is released from the adduct species into the solution and therefore the polymer-dye adduct species $[CL.D]_S$ is stable. The data show that the total percentage of dye with respect to that in the solid polymer phase that is released back into solution after repeat washes is 11.4 %. The dye that is lost during these repeated cycles is attributed to free dye that was present in the solid polymer compartment. The assumption is made for the derivation of Equation 7.12 that the degree of dye

that is present in the free-volume in the solid polymer compartment is negligible as a fraction of the total concentration of polymer and dye in the system. To ensure the validity of this assumption then for all further experimental work the initial concentration of dye $[D_0]_L$ is always below or equal to $1.9x10^{-5}$ M, therefore the percentage of dye in the free-volume is maintained as less than 11.4 % of the dye in solid polymer phase.

7.2.2.5 Calculation of K_S for cross-linked poly(N-vinyl pyrrolidone)

The validity of the factors that are used to determine K_S and K_P from experimental procedures by static sorption is dependent on several factors:

The solution of three variables is required to determine the value of K_S from static sorption. These are, the total number of binding sites in the cross-linked polymer $[CL_0]_S$, the initial dye concentration $[D_0]_L$ and the amount of free dye remaining in the liquid compartment $[D]_L$ at equilibrium is established.

In all cases the concentration of initial dye stock solution $[D_0]_L$ was determined by measuring the λ-max for the stock solution. The concentration of the free dye in the liquid phase $[D]_L$ was determined by measuring the λ-max of the supernatant solution after the removal of the polymer and polymer/dye adduct using centrifugation.

The total number of binding sites in the cross-linked polymer $[CL_0]_S$ was determined for cross-linked poly(N-vinyl pyrrolidone) (PVP-CL). $[CL_0]_S$ is calculated from the volume fraction of the polymer with respect to the total solution assuming that all monomer units in the polymer can act as effective dye-binding sites.

The relative molecular mass of N-vinyl pyrrolidone monomer is 111.14 g mol^{-1} and the density of the cross-linked PVP is 1.040 g ml^{-1} [7].

Therefore, $$\frac{g\ ml^{-1}}{g\ mol^{-1}} = \frac{1.040}{111.14} = 9.3576 \times 10^{-2}\ mol\ ml^{-1} = [CL_0]_S$$

The dye-binding equilibrium constant K_S for the water-insoluble cross-linked poly(N-vinyl pyrrolidone) polymer with the anionic azo-dye, Direct Red 80 was determined by static sorption. A simple test for the determination of K_S was developed. A known concentration aqueous stock solution of Direct Red 80 azo-dye was prepared, into which a known amount of insoluble cross-linked poly(N-vinyl pyrrolidone) polymer was added. The mixture was stirred for 25 minutes until dye-binding equilibrium had been established. Centrifugation of the mixture allowed the removal of the polymer and polymer/dye adduct species from the remaining supernatant dye solution. The λ-max at 534 nm of the supernatant dye solution was measured to determine the amount of free dye remaining in solution after dye-binding equilibrium had been established.

Tests were performed for a series of different [polymer]/[dye] ratios. Full details of the experimental procedure are given in the experimental chapter 9. Stock solution of dye was prepared with deionised water to give a total dye concentration in solution of ~1.9×10^{-5} mol l^{-1}. To a 50 ml aliquot of dye stock solution a known amount of cross-linked poly(N-vinyl pyrrolidone) (PVP-CL) was added. The resulting suspension was agitated for 25 minutes and then the supernatant solution was isolated by centrifugation and the λ-max at 534 nm was determined. Table 7.4 lists the range of concentrations for which K_S that was determined for the cross-linked PVP.

Table 7.4 Concentration parameters for the determination of K_S for PVP-CL by static sorption

PVP-CL (gl^{-1})	PVP-CL (g)	Volume of PVP-CL (ml)	$\varphi = \frac{\text{Volume of PVP-CL}}{\text{Volume of liquid}}$ $X10^{-2}$
10	0.5	0.4808	0.962
20	1.0	0.9615	1.923
40	2.0	1.9231	3.846
60	3.0	2.8846	5.770
80	4.0	3.8462	7.692

For each test the total concentration of dye $[D_0]_L = 1.99 \times 10^{-5}$ mol l^{-1}, the total concentration of available binding sites $[CL_0]_S = 9.36$ mol l^{-1} and the concentration of free dye after equilibrium $[D]_L$ were known. From these parameters the value of $[CL.D]_S$ was calculated using Equation 7.12.

The calculation of K_S was then performed using Equation 7.3. The data for the calculation of K_S for each experiment is given in Table 7.5.

Table 7.5 Determined values of K_S for PVP-CL with Direct Red 80 for a range of [Dye]/[PVP-CL] ratios

PVP-CL (gl^{-1})	φ $x10^{-2}$	$[D]_L$ (mol l^{-1}) $x10^{-6}$	$[CL.D]_S$ (mol l^{-1}) $x10^{-4}$	K_S
10	0.962	2.439	16.13	70.69
20	1.923	1.504	8.50	60.40
40	3.846	0.720	4.43	65.75
60	5.770	0.519	2.29	47.15
80	7.692	0.377	1.81	51.31
Average K_S				59.06

The average value of the dye-binding constant for the cross-linked water-insoluble poly(N-vinyl pyrrolidone) is 59.06. The determined value of K_S is higher than the reported literature value, where K_S is 24 [7]. The low degree of scatter in the data collected suggests that some differences are present between the data calculated here and those quoted in the literature [7]. The determined value of K_S may be different due to the source of the cross-linked polymer that is used and due to the new factor that is introduced in Equation 7.12. This takes into the account the degree of dye that is present in the sold polymer compartment as free dye. The degree of cross-linking of the PVP-CL polymer will affect the value of K_S and polymer used here is not obtained from the same source as that used in the literature. The average value of K_S that is determined here will be used for all future calculations for the determination of K_P.

7.2.3 Determination of the dye-binding constant for a water-soluble polymer, K_P from static sorption

K_P is the dye-binding constant for a water-soluble polymer in the liquid phase. K_P is defined as the ratio of the total occupied binding sites $[P.D]_L$ with respect to the product of the free binding site concentration for the water-soluble polymer $[P]_L$ and the free dye concentration in the liquid phase $[D']_L$. This is analogous to the definition of K_S that was given in equation (7.1)

$$K_P = \frac{[P.D]_L}{[D']_L[P]_L} \qquad (7.14)$$

$[P]_L$ is the total free binding site concentration for the polymer and is equal to the number of occupied binding sites at equilibrium $[P.D]_L$ subtracted from the total number of binding sites in the polymer before the addition of dye $[P_0]_L$. This is analogous to the derivation given in terms of K_S in Equation 7.2.

$$[P]_L = [P_0]_L - [P.D]_L \qquad (7.15)$$

Substituting (7.15) into (7.14) gives:

$$K_P = \frac{[P.D]_L}{[D']_L([P_0]_L - [P.D]_L)} \qquad (7.16)$$

The total concentration of dye in the liquid polymer compartment $[D]_{F,L}$ is considered to be composed of dye in the bound state $[P.D]_L$ and free dye in the liquid phase $[D]_L$. The homogeneity of the system means that the dye present in the liquid polymer compartment is combined with the total free dye in the system.

$$[D]_{F,L} = [P.D]_L + [D]_L \qquad (7.17)$$

For the heterogeneous system, where an insoluble cross-linked polymer binds with a soluble dye then the absorption of the supernatant solution gives the concentration of the free dye in the solution after dye-binding. For a homogeneous system where a water-soluble polymer binds with a soluble dye then the liquid phase is composed of dye in the bound state $[P.D]_L$ and free dye $[D']_L$. The absorption of the system can not be used to directly determine the concentration of the free dye due to peak overlap. A method is required to determine the free dye concentration after binding with the water-soluble polymer to allow the calculation of the dye-binding constant, K_P.

7.2.4 Combination of expressions for water-soluble and water-insoluble polymer components to allow the determination of K_P from static sorption

The absorption at the λ-max for the free dye of a solution containing a water-soluble polymer and a dye gives a factor relating to the combined concentration of the free dye and the bound dye in solution. The actual concentration of the free dye in solution is not known due to peak overlap resulting from bathochromic shifts in the spectrum that result from dye-binding. The addition

of a cross-linked polymer to a dye solution containing a water-soluble polymer produces a decrease in the absorption of the resulting supernatant solution. It is assumed that dye binding of the cross-linked polymer may only occur with free dye and not with dye bound to the water-soluble polymer. The absorption of the supernatant solution may therefore be used to calculate the concentration of free dye that is present in the solution before the addition of the cross-linked polymer when the dye binding constant for the cross-linked polymer with the test dye, K_S is known. Equation 7.18 gives the total dye concentration in the liquid phase including bound dye to water-soluble polymer after dye-binding with both water-soluble polymer and cross-linked polymer, $[D]_{F,L}$.

$$[D]_{F,L} = [P.D]_L + [D]_L = [D_0]_L . \frac{A_2}{A_1} \qquad (7.18)$$

A_1 represents the absorption of the dye solution containing water-soluble polymer and A_2 represents the absorption of the dye solution containing both cross-linked polymer and water-soluble polymer. $[D_0]_L$ is the total concentration of dye in solution before the addition of the polymers and $[D]_L$ is the concentration of free dye in the liquid phase after the addition of the cross-linked polymer. $[P.D]_L$ is the concentration of water-soluble polymer bound to dye in the liquid phase. The product of the ratio of the absorbances with the initial dye concentration gives the concentration of free dye that remains in the liquid compartment after binding. This concentration of the free dye can be used to determine the initial free dye concentration that was present before binding with the cross-linked polymer when the dye binding constant for the cross-linked polymer is known.

Equation 7.16 gave the dye-binding equilibrium constant for the water-soluble polymer in terms of the free dye concentration $[D']_L$, the initial polymer concentration $[P_0]_L$ and the concentration of occupied sites in the polymer after equilibration $[P.D]_L$.

$$K_P = \frac{[P.D]_L}{[D']_L([P_0]_L - [P.D]_L)} \qquad (7.16)$$

Substituting for [P.D] with equation (7.17) gives:

$$K_P = \frac{[D]_{F,L} - [D']_L}{[D']_L([P_0]_L - \{[D]_{F,L} - [D']_L\})} \qquad (7.19)$$

An expression for the determination of $[D']_L$ is now required. $[D']_L$ represents the free dye that is present in the liquid compartment after equilibrium is established with the water-soluble polymer. A direct measurement of the value of $[D']_L$ is not possible due to overlap in the absorption spectra for free dye and that for the water-soluble dye-polymer adducts. The addition of cross-linked polymer to water-soluble polymer/dye solution allows the measurement of the reduction in absorption of the free dye in solution and taking into consideration the dye-binding equilibrium constant for the cross-linked polymer, K_S an expression for $[D']_L$ is derived.

Equation 7.3 is rearranged in terms of the mass of dye present in the system. D'_L represents the mass of the free dye that is present before binding occurs with the cross-linked polymer: this is equal to the mass of free dye after equilibrium has been established between the water-soluble polymer and the dye.

$$D'_L = \frac{CL.D_S}{K_S(CL_{0,S} - CL.D_S)} \qquad (7.20)$$

Dividing throughout by the volume in the liquid phase gives:

$$\frac{D'_L}{V_L} = \frac{\frac{CL.D_S}{V_L}}{\frac{K_S(CL_{0,S} - CL.D_S)}{V_L}} \qquad (7.21)$$

The mass of the cross-linked polymer/dye species $CL.D_S$ is equal to the mass of the dye in the liquid phase subtracted from the initial dye mass (Equation 7.22).

$$CL.D_S = D_{0,L} - D_{F,L} \qquad (7.22)$$

Substitution of Equation 7.22 into 7.21 gives an expression in terms of the dye in the liquid phase that was measured in the system containing both water-soluble polymer and cross-linked water-insoluble polymer D_F.

$$\frac{D'_L}{V_L} = \frac{\frac{(D_{0,L} - D_{F,L})}{V_L}}{\frac{K_S(CL_{0,S} - \{D_{0,L} - D_{F,L}\})}{V_L}} \qquad (7.23)$$

$$[D']_L = \frac{\frac{(D_{0,L} - D_{F,L})}{V_L}}{\frac{K_S(CL_{0,S} - \{D_{0,L} - D_{F,L}\})}{V_L}} \qquad (7.24)$$

Equation 7.24 is given in terms of the concentration of the dye throughout the system. The phase ratio is introduced to allow the initial mass of binding sites in the cross-linked polymer $CL_{0,S}$ to be determined in terms of the concentration in the liquid phase. All other components exist in the liquid phase and are considered as their respective concentrations.

$$[D']_L = \frac{([D_O]_L - [D]_{F,L})}{K_S.(\varphi[CL_0]_S - \{[D_O]_L - [D]_{F,L}\})} \qquad (7.25)$$

7.2.5 Calculation of K_P for a water-soluble polymer in deionised water

The following procedure was used to determine the dye-binding constant, K_P for all water-soluble polymers in deionised water, where no surfactant was present.

A known concentration stock solution of Direct Red 80 dye was prepared. To a 50 ml aliquot of this stock solution a known amount of water-soluble polymer was added. The mixture was agitated for 25 minutes and then the λ-max at 534 nm was determined. To the resulting solution an accurately weighed sample of a water-insoluble cross-linked polymer of known K_S was added. For all experiments performed herein the cross-linked polymer used in all cases was cross-linked poly(N-vinyl pyrrolidone) (PVP-CL). The mixture was then agitated for a further 25 minutes and then the supernatant solution was isolated by centrifugation and the λ-max at 534 nm was determined.

7.2.5.1 Calculation of K_P for water-soluble PVP K-25 (1.4)

The calculation of the dye-binding constant, K_P for a water-soluble poly(N-vinyl pyrrolidone) homopolymer, PVP (1.4) K-25 (Mn~25000 Da) was performed. The experimental data and calculation of K_P for a range of different [water-soluble polymer]/[dye] ratios were determined.

A stock solution of Direct Red 80 dye (~1.9×10^{-5} M) was accurately prepared into 1 litre of deionised water. The UV/Visible spectrum of this stock solution was determined between 400 and 650 nm and the absolute concentration of dye in solution was determined with reference to the calibration plot given in Figure 7.0.

The water-soluble test polymer was accurately weighed into 8 conical flasks and to each of these a known volume of the dye stock solution was accurately pipetted to give a series of dye solutions containing different concentrations of polymer. Table 7.6 lists the different polymer solutions that were prepared.

Table 7.6 Water-soluble polymer solutions prepared in dye solution ($1.9x10^{-5}$ M)

Solution	Water-soluble polymer (g)	Dye stock solution (l)	Polymer ($g.l^{-1}$)
A	0	0.05	0
B	0.25	0.05	5
C	0.05	0.05	1
D	0.025	0.05	0.5
E	0.01	0.05	0.2
F	0.005	0.05	0.1
G	0.0125	0.250	0.05
H	0.0025	0.250	0.01

50 ml of each of the polymer solutions was accurately pipetted into a 250 ml conical flask. Each flask was sealed with a rubber bung and then all of the samples were shaken at room temperature for 25 minutes. After agitation the UV/visible spectrum for each solution was determined between 400 and 650 nm. The absorption of these solutions at 534 nm (A_1) was calculated.

To each solution of water-soluble polymer 2.0 g of insoluble cross-linked poly(N-vinyl pyrrolidone) (PVP-CL) of known dye binding constant, K_S was accurately added. The suspensions of cross-linked polymer in the water-soluble polymer/dye solution were then shaken for a further 25 minutes at room temperature. The supernatant solutions were then isolated by centrifugation at 5000 rpm for 30 minutes. The UV/Visible spectra of these samples were

determined between 400-650 nm. The absorption of these solutions at 534 nm (A_2) was calculated. The calculation of the dye-binding constant, K_P is outlined in detail for each data point for PVP, K25. For all subsequent calculations of K_P for water-soluble polymers by static sorption the method of calculation used is identical to that outlined here.

The concentration of the dye stock solution was determined by using the equation of the line calculated from the calibration plot for Direct Red 80 in aqueous solution. Equation 7.26 is the equation of the line rearranged in terms of the dye concentration to allow the determination of the concentration of all unknown dye solutions.

$$[D_0]_L = \left(\frac{A - 0.01288}{106506}\right) \qquad (7.26)$$

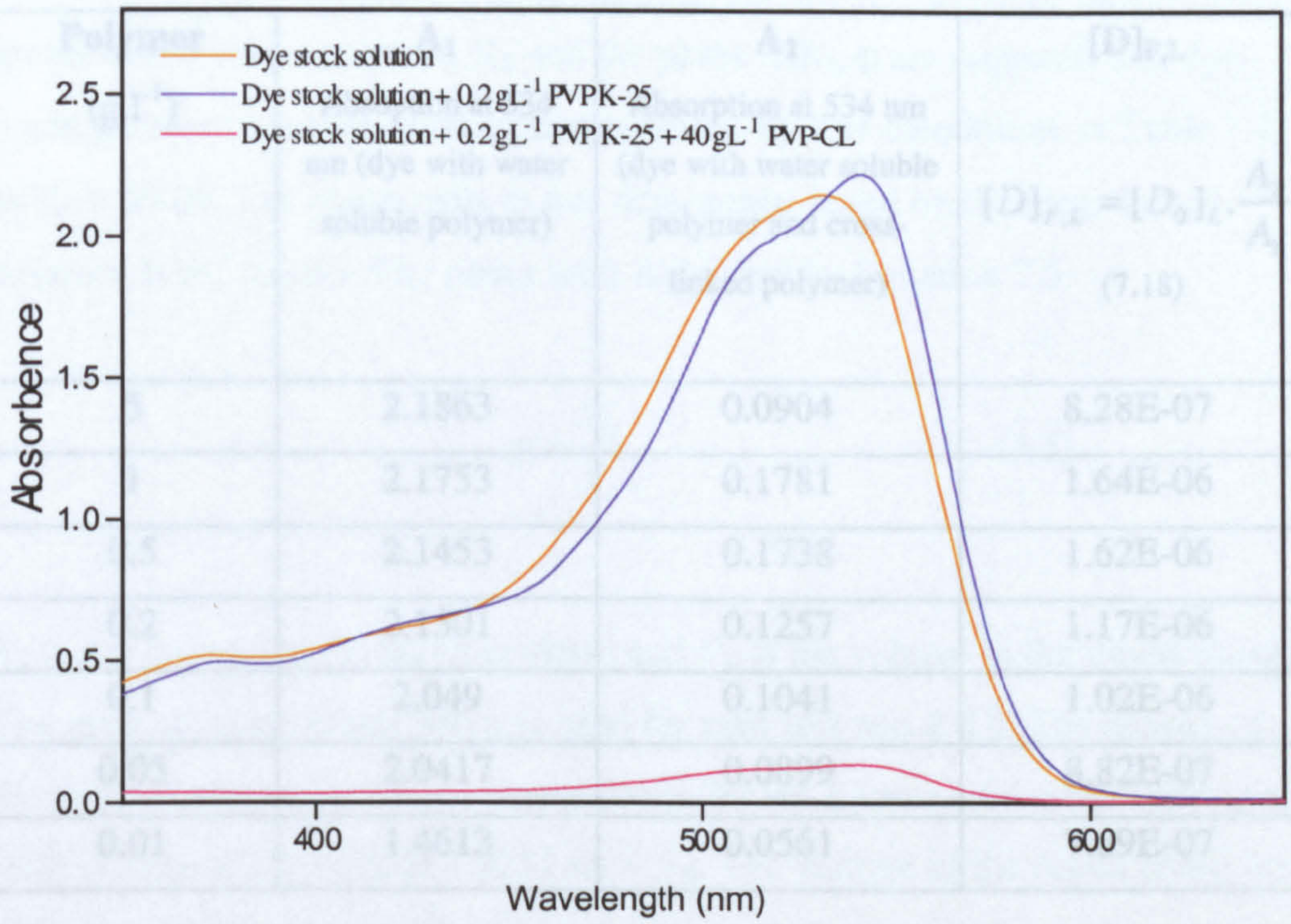
$[D_0]_L$ is the concentration of the dye in solution and A is the absorption at 534 nm. The absorption of the dye stock solution at 534 nm was determined to be 2.1459. The concentration of dye in the solution was determined using equation 7.26.

$$[D_0]_L = \left(\frac{2.1459 - 0.01288}{106506}\right) = 2.0027x10^{-5} mol.l^{-1}$$

Table 7.6 gives the determined absorption of the initial dye stock solution and the absorbances of all of the solutions when water-soluble polymer was added and when cross-linked polymer was added. The concentration of the free dye remaining in the liquid phase after dye binding $[D]_{F,L}$ was calculated from Equation 7.18.

The UV/Visible spectra for the polymer stock solution and for the stock solution with the addition of water-soluble polymer and with the addition of water-soluble polymer and cross-linked polymer are given in Figure 7.9.

Figure 7.9 UV/Visible spectra for the dye stock solution with the addition of the water-soluble polymer, PVP K-25 and with the addition of the cross-linked polymer, PVP-CL



The spectra show that the dye stock solution contains only one major absorption band at 534 nm. The addition of the water-soluble polymer, PVP K-25 creates a bathochromic shift in the absorption band to higher wavenumber. This new band is assigned as the newly formed dye/polymer adduct. The optical density of this new absorption band was found to be invariant with the concentration of the water-soluble PVP homopolymer that was added. The addition of the cross-linked polymer is shown to dramatically reduce the absorption of the band at 534 nm. The reduction in absorption is the result of dye-binding with the cross-linked polymer species to form insoluble dye/polymer adduct and therefore a reduction in the overall dye content in the aqueous phase occurs.

Table 7.7 Data from the dye-binding of water-soluble polymer and cross-linked polymer with PVP K-25 to determine the concentration of dye remaining in the liquid phase

Polymer ($g.l^{-1}$)	A_1 Absoption at 534 nm (dye with water soluble polymer)	A_2 Absorption at 534 nm (dye with water soluble polymer and cross-linked polymer)	$[D]_{F,L}$ $[D]_{F,L} = [D_0]_L . \frac{A_2}{A_1}$ (7.18)
5	2.1863	0.0904	8.28E-07
1	2.1753	0.1781	1.64E-06
0.5	2.1453	0.1738	1.62E-06
0.2	2.1501	0.1257	1.17E-06
0.1	2.049	0.1041	1.02E-06
0.05	2.0417	0.0899	8.82E-07
0.01	1.4613	0.0561	7.69E-07

The concentration of dye that is present in the liquid phase is composed of free dye $[D]_L$ and dye that is bound to the water-soluble polymer species $[P.D]_L$. The concentration of the cross-linked polymer-dye species $[CL.D]_S$ can be calculated from Equation 7.22.

$$CL.D_S = D_{0,L} - D_{F,L} \qquad (7.22)$$

Dividing throughout by the volume in the liquid phase gives Equation 7.22 in terms of the relative concentrations.

$$[CL.D]_S = [D_0]_L - [D]_{F,L} \qquad (7.27)$$

The values of $[D_0]_L$ and $[D]_{F,L}$ are substituted into Equation 7.25 to allow the evaluation of the concentration of the free dye that remains in solution after the addition of water-soluble polymer $[D']_L$.

$$[D']_L = \frac{([D_O]_L - [D]_{F,L})}{K_S(\varphi[CL_0]_S - \{[D_O]_L - [D]_{F,L}\})} \quad (7.25)$$

To calculate the concentration of $[D']_L$ the values of the dye-binding constant for the cross-linked polymer, K_S and the phase ratio, φ are required. The dye-binding constant for the cross-linked polymer, K_S was determined in Table 7.4 as $K_S = 59.06$. The phase ratio, φ was determined based on the cross-linked polymer in the system. The phase ratio is defined by Equation 7.5.

$$\varphi = \frac{V_S}{V_L} \quad (7.5)$$

V_S is the volume in the polymer phase and V_L is the volume in the liquid phase. The mass of cross-linked polymer used for each test was 2.0 g. The density of the cross-linked poly(N-vinyl pyrrolidone) (PVP-CL) was 1.04 g ml^{-1}, giving a total volume of PVP-CL of 1.9231 ml = V_S. The volume of the liquid phase for each test used was 50 ml. Therefore the value of the phase ratio, φ for each test was:

$$\varphi = \frac{V_S}{V_L} = \frac{1.9231}{50} = 3.85x10^{-2}$$

Table 7.7 gives the data for samples B to H for the calculation of the concentration of the free dye that remains in solution after the addition of water-soluble polymer $[D']_L$.

Table 7.8 Data for the calculation of the free dye that remains in solution after the addition of water-soluble polymer $[D']_L$

Polymer ($g.l^{-1}$)	$[D]_{F,L}$	$[CL.D]_S$ $[CL.D]_S = [D_0]_L - [D]_{F,L}$ (7.27)	$[D']_L$ $[D']_L = \frac{([D_O]_L - [D]_{F,L})}{K_s(\phi[CL_0]_S - \{[D_O]_L - [D]_{F,L}\})}$ (7.25)
5	8.28×10^{-7}	1.92×10^{-5}	9.04×10^{-7}
1	1.64×10^{-6}	1.84×10^{-5}	8.65×10^{-7}
0.5	1.62×10^{-6}	1.84×10^{-5}	8.66×10^{-7}
0.2	1.17×10^{-6}	1.89×10^{-5}	8.87×10^{-7}
0.1	1.02×10^{-6}	1.90×10^{-5}	8.95×10^{-7}
0.05	8.82×10^{-7}	1.92×10^{-5}	9.01×10^{-7}
0.01	7.69×10^{-7}	1.93×10^{-5}	9.06×10^{-7}

The value of $[D']_L$ is then substituted into Equation 7.19 to calculate the dye-binding constant for the water-soluble polymer.

$$K_P = \frac{[D]_{F,L} - [D']_L}{[D']_L([P_0]_L - \{[D]_{F,L} - [D']_L\})} \qquad (7.19)$$

$[P_0]_L$ is the initial concentration of binding sites from the water-soluble polymer in the liquid phase. $[P_0]_L$ is calculated assuming that each repeat unit in the polymer can act as a binding site. The total mass of polymer divided by the molecular weight of the polymer repeat unit gives the initial concentration of binding sites in the liquid polymer phase, for poly(N-vinyl pyrrolidone) the relative molecular mass (rmm) of the repeat unit this is 111.12 g mol^{-1}. For sample B where 0.5 g of polymer is added:

$$\frac{polymer}{rmm} = [P_0]_L = \frac{0.5g}{111.12g.mol^{-1}} = 0.045.mol$$

The value of $[P_0]_L$ has been calculated for each sample respectively. Table 7.8 gives the data for the calculation of the dye-binding constant for the water-soluble polymer.

Table 7.9 Data for the calculation of the dye-binding constant, K_P for the water-soluble polymer, PVP K-25

Polymer ($g.l^{-1}$)	$[D]_{F,L}$	$[D']_L$	$[P_0]_L$	**K_P** $K_P = \frac{[D]_{F,L} - [D']_L}{[D']_L([P_0]_L - \{[D]_{F,L} - [D']_L\})}$ (7.19)
5	8.28×10^{-7}	9.04×10^{-7}	4.5×10^{-2}	0
1	1.64×10^{-6}	8.65×10^{-7}	9.0×10^{-3}	99.5
0.5	1.62×10^{-6}	8.66×10^{-7}	4.5×10^{-3}	194.2
0.2	1.17×10^{-6}	8.87×10^{-7}	1.8×10^{-3}	177.7
0.1	1.02×10^{-6}	8.95×10^{-7}	9×10^{-4}	153.0
0.05	8.82×10^{-7}	9.01×10^{-7}	4.5×10^{-4}	-46.7
0.01	7.69×10^{-7}	9.06×10^{-7}	9×10^{-5}	-1680.2

A plot of the dye-binding constant K_P versus the ratio of dye to dye-binding sites in the water-soluble polymer PVP K-25, $[D_0]_L/[P_0]_L$ is given in Figure 7.10. The data point for 0.01 g l^{-1} of polymer has been omitted for clarity.

Figure 7.10 Plot of the dye-binding constant, K_P for the water-soluble PVP K-25 polymer versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$

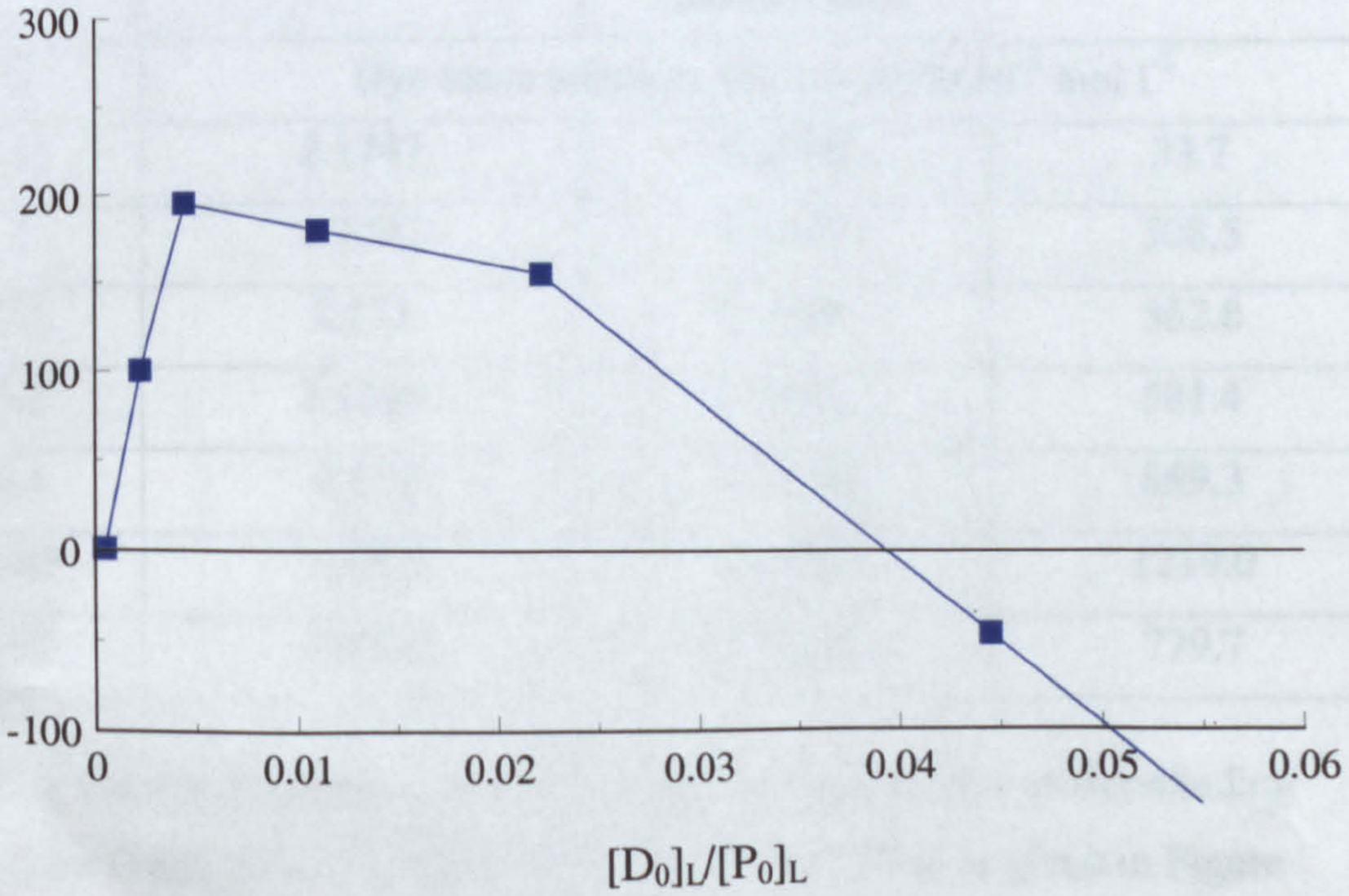


Figure 7.10 shows that, unlike cross-linked polymers, the value of the dye-binding constant, K_P for a water-soluble polymer is dependent on the concentration of the available binding sites, $[P_0]_L$.

7.2.5.2 Calculation of K_P for water-soluble PVP K-30

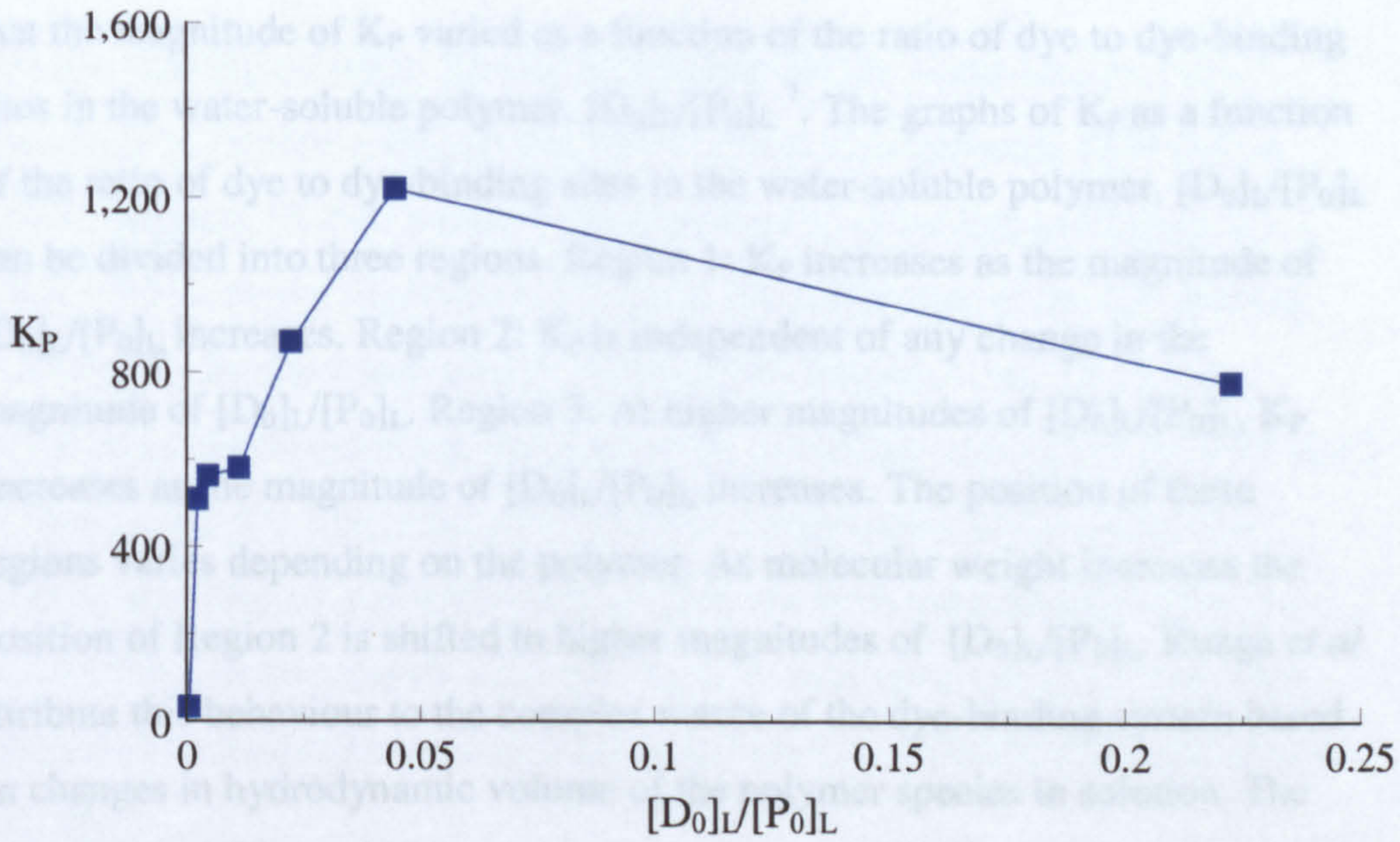
The dye-binding constant, K_P was determined for another water-soluble poly(N-vinyl pyrrolidone) homopolymer, PVP K-30 with a higher average molecular weight (Mn ~40000 Da) to compare how the dye-binding constant varies with the molecular weight of the polymer species. Table 7.10 gives the experimental data for the calculation of the dye-binding constant, K_P for the water-soluble polymer PVP K-30. All calculations were performed using the same procedure as outlined for PVP K-25 in Section 7.2.5.1.

Table 7.10 Experimental data for the calculation of the dye-binding constant, K_P for the water-soluble polymer PVP K-30

Polymer ($g.l^{-1}$)	A_1 Absorption at 534 nm (dye with water soluble polymer)	A_2 Absorption at 534 nm (dye with water soluble polymer and cross-linked polymer)	K_P
0	Dye stock solution, $[D_0]_L = 2.02 \times 10^{-5}$ mol l^{-1}		
5	2.1747	0.2308	33.7
1	2.1327	0.4431	508.5
0.5	2.131	0.3036	562.8
0.2	2.1229	0.1864	581.4
0.1	2.114	0.1635	869.3
0.05	2.0992	0.1425	1219.0
0.01	2.0904	0.1002	779.7

A plot of the dye-binding constant K_P versus the ratio of dye to dye-binding sites in the water-soluble polymer PVP K-30, $[D_0]_L/[P_0]_L$ is given in Figure 7.11.

Figure 7.11 Plot of the dye-binding constant, K_P for the water-soluble PVP K-30 polymer versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$



The data show that the relative dye-binding constant, K_P for a water-soluble poly(N-vinyl pyrrolidone) homopolymer increases as the molecular weight of the polymer is increased from 25000 to 40000 Da. The dye-binding data for PVP K-30 (Mn ~ 40000) and PVP K-17 (Mn ~ 10 000) by static sorption have been previously reported in the literature. Table 7.11 gives a comparison of the data obtained by Runge *et al* for PVP K-17 and PVP K-30 with the experimental data obtained in this study [7].

Table 7.11 Comparison of data for the dye-binding constant, K_P of water soluble polymers by static sorption studies

Polymer	K_P ($[D_0]_L/[P_0]_L = 1x10^{-2}$)	
	Experimental data	**Data from Runge *et al***
PVP K-17	-	1000
PVP K-25	180	-
PVP K-30	580	1500

The dye-binding constant is shown to increase with increasing degree of polymerisation of the polymer, which is in agreement with previous studies [1,7-9]. The data obtained from this research and the data reported by Runge *et al* found that the magnitude of K_P varied as a function of the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$ [7]. The graphs of K_P as a function of the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$ can be divided into three regions. Region 1: K_P increases as the magnitude of $[D_0]_L/[P_0]_L$ increases. Region 2: K_P is independent of any change in the magnitude of $[D_0]_L/[P_0]_L$. Region 3: At higher magnitudes of $[D_0]_L/[P_0]_L$, K_P decreases as the magnitude of $[D_0]_L/[P_0]_L$ increases. The position of these regions varies depending on the polymer. As molecular weight increases the position of Region 2 is shifted to higher magnitudes of $[D_0]_L/[P_0]_L$. Runge *et al* attribute this behaviour to the complex nature of the dye-binding system based on changes in hydrodynamic volume of the polymer species in solution. The calculation of the dye-binding constant for a water-soluble polymer is based on the assumption that each repeat unit can act as a dye-binding site [7]. The PVP homopolymer adopts a coiled conformation in aqueous solution and therefore some of the binding sites are trapped in the centre of the polymer coil and are not available for binding with the free dye. As binding of the homopolymer with dye occurs at the exterior of the polymer coil then the dye/polymer adduct exhibits polyelectrolyte behaviour [8-11] and coil extension occurs [12-15]. The increase in coil extension increases the effective concentration of the available binding sites and this is observed as a rise in the dye-binding constant of the polymer species. At high concentrations of dye to dye-binding site concentration then electrostatic repulsion in the charged polymer chain is believed to inhibit dye-binding and this is observed as a decrease in the dye-binding constant K_P [16].

7.2.5.3 Calculation of K_P for water-soluble PDMAEMA homopolymer (2.1)

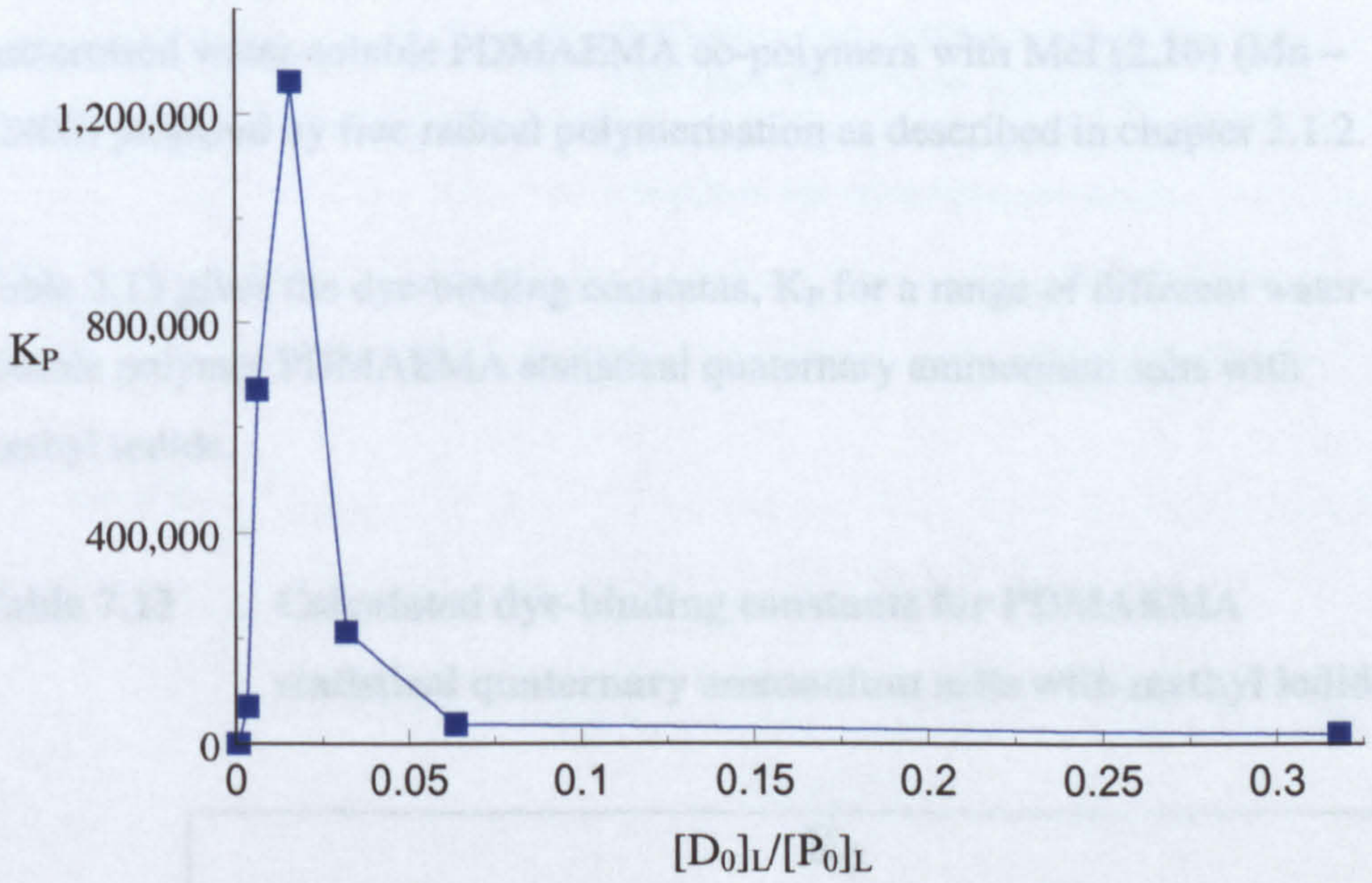
The dye-binding constant, K_P was determined for the water-soluble poly(2-dimethylamino)ethyl methacrylate PDMAEMA homopolymer (**2.1**) (Mn = 22400) prepared by free radical polymerisation as described in Chapter 2.1.1. Table 7.12 gives the experimental data for the calculation of the dye-binding constant, K_P for the water-soluble PDMAEMA homopolymer (**2.1**). All calculations were performed using the same procedure as outlined for PVP K-25 in Section 7.2.5.1. The phase ratio and the concentration of the initial dye-binding sites $[P_0]_L$ in the water-soluble polymer were determined for the new PDMAEMA homopolymer and from these an analogous series of tests were performed to determine the dye-binding constant for PDMAEMA with Direct Red 80.

Table 7.12 Experimental data for the calculation of the dye-binding constant, K_P for the water-soluble polymer PDMAEMA (Mn = 22400)

Polymer ($g.l^{-1}$)	A_1 Absorption at 534 nm (dye with water soluble polymer)	A_2 Absorption at 534 nm (dye with water soluble polymer and cross-linked polymer)	K_P
0	Dye stock solution, $[D_0]_L = 2.02 \times 10^{-5}$ mol l^{-1}		
5	2.1311	0.6016	230
1	2.1409	2.0441	71000
0.5	2.1442	2.123	673000
0.2	2.1848	2.1558	1261000
0.1	2.1224	1.8303	213600
0.05	1.946	0.7346	38200
0.01	1.7789	0.1679	19400

A plot of the dye-binding constant K_P versus the ratio of dye to dye-binding sites in the water-soluble polymer PDMAEMA homopolymer, $[D_0]_L/[P_0]_L$ is given in Figure 7.12.

Figure 7.12 Plot of the dye-binding constant, K_P for the water-soluble PDMAEMA homopolymer (Mn = 22400) versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$



The data show that the maximum value of K_P obtained for PDMAEMA in comparison to the PVP homopolymers is several orders of magnitude greater. This shows that the PDMAEMA homopolymer has a strongly favoured binding interaction with Direct Red 80 in comparison to PVP. The graph of K_P versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$ can be separated into three regions. Region 1: K_P increases as the magnitude of $[D_0]_L/[P_0]_L$ increases. Region 2: A point where K_P is independent of any change in the magnitude of $[D_0]_L/[P_0]_L$. Region 3: K_P decreases as the magnitude of $[D_0]_L/[P_0]_L$ increases. The maximum value of K_P is found at a lower ratio of dye to dye-binding sites ($[D_0]_L/[P_0]_L = 1.59 \times 10^{-2}$) than that found for the PVP polymers ($[D_0]_L/[P_0]_L = 2.23 \times 10^{-1}$). A study of the dye-binding nature of

quaternised PDMAEMA polymers was performed to help understand the interaction of PDMAEMA with Direct Red 80.

7.2.5.4 Calculation of K_P for a series of statistically quaternised water-soluble PDMAEMA co-polymers (2.10) with MeI

The dye-binding constant, K_P was determined for a series of statistically quaternised water-soluble PDMAEMA co-polymers with MeI (**2.10**) (Mn ~ 22400) prepared by free radical polymerisation as described in chapter 2.1.2.

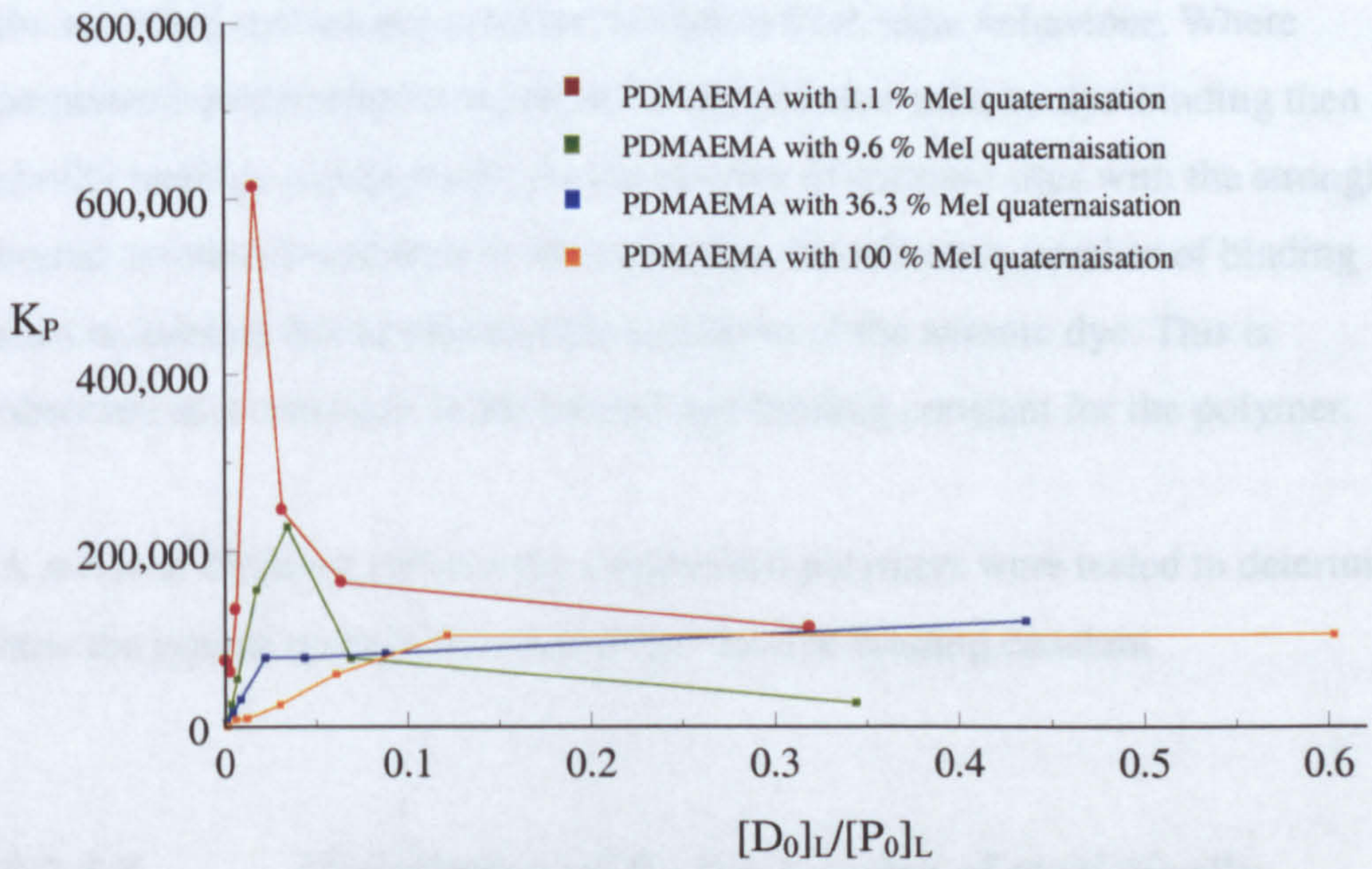
Table 7.13 gives the dye-binding constants, K_P for a range of different water-soluble polymer PDMAEMA statistical quaternary ammonium salts with methyl iodide.

Table 7.13 Calculated dye-binding constants for PDMAEMA statistical quaternary ammonium salts with methyl iodide

	K_P PDMAEMA with methyl iodide quaternisation			
Polymer ($g.l^{-1}$)	**1.1%**	**9.6%**	**36.3%**	**100%**
5	74400	5600	6200	700
1	62300	26100	16400	8600
0.5	132500	54400	31300	9700
0.2	612000	155200	74300	25100
0.1	244600	226200	78700	60000
0.05	163300	78300	83400	103600
0.01	111700	27600	119800	104800

The plots of the dye-binding constant K_P versus the ratio of dye to dye-binding sites in the water-soluble polymer for the PDMAEMA statistical quaternary ammonium salts with MeI, $[D_0]_L/[P_0]_L$ are given in Figure 7.13.

Figure 7.13 Plot of the dye-binding constant, K_P for the water-soluble PDMAEMA statistical quaternary ammonium salts with methyl iodide versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$



The data show that, as the degree of quaternisation is increased, the maximum magnitude of the dye-binding constant K_P is reduced and that the maximum dye-binding constant is shifted to a higher ratio of the dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$.

The neutral PDMAEMA homopolymer gives the largest value of K_P. As is the case of PVP with dye, the formation of the dye-polymer adduct with PDMAEMA creates a charged macromolecular species. The PDMAEMA homopolymer is thought to exhibit similar aqueous solution properties to PVP. In a non-ionic environment the polymer forms a compact coil conformation and, as the degree of charge along the polymer is increased, then the polymer forms an extended coil. As the polymer elongates in solution then the effective number

of dye binding sites increases and the dye-binding constant is observed to increase. For systems where permanent charge is incorporated into the polymer the effect of adsorbing dye on to the polymer will have a lesser effect on the effective dye binding site concentration than for the neutral PDMAEMA homopolymer in solution. This is observed as a shift to a higher ratio of the dye to dye-binding site concentration in the water-soluble polymer, $[D_0]_L/[P_0]_L$ where the maximum absorption occurs.

As the degree of quaternisation increases then electrostatic repulsion between the adsorbed species accounts for deviation from ideal behaviour. Where permanent quaternisation is present in the polymer prior to dye-binding then a similar analogy can be made. As the number of cationic sites with the strongly bound anionic counterions is increased then the effective number of binding sites is reduced due to electrostatic repulsion of the anionic dye. This is observed as a reduction in the overall dye-binding constant for the polymer.

A series of different statistically quaternised polymers were tested to determine how the type of quaternisation affected the dye-binding constant.

7.2.5.5 Calculation of K_P for a series of statistically quaternised water-soluble PDMAEMA co-polymers (2.11) with sodium chloroacetate

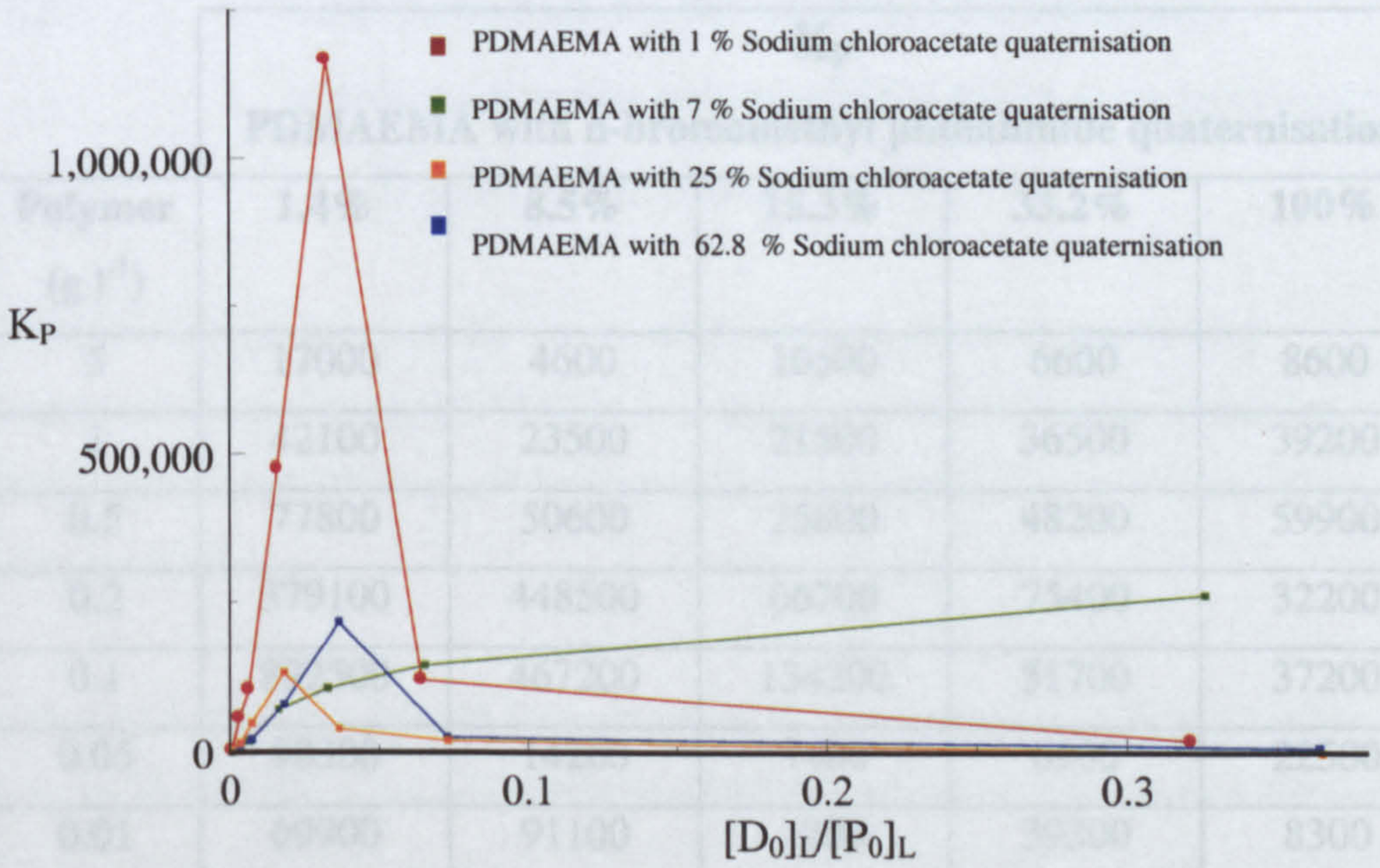
The dye-binding constant, K_P was determined for a series of statistically quaternised water-soluble PDMAEMA co-polymers with sodium chloroacetate **(2.11)** (Mn ~ 22400) prepared by free radical polymerisation as described in chapter 2.1.3.

Table 7.14 gives the dye-binding constants, K_P for a range of different water-soluble polymer PDMAEMA statistical quaternary ammonium salts with sodium chloroacetate.

Table 7.14 Calculated dye-binding constants for PDMAEMA statistical quaternary ammonium salts with sodium chloroacetate

	K_P PDMAEMA with Sodium chloroacetate quaternisation			
Polymer ($g.l^{-1}$)	**1%**	**7%**	**25%**	**61.9%**
5	0	-2700	0	2600
1	53900	6100	7100	11900
0.5	102600	15100	17800	45100
0.2	474700	68300	77300	130500
0.1	1167800	104200	215900	35500
0.05	118200	142400	21700	15600
0.01	16200	261100	4400	-4900

Figure 7.14 Plot of the dye-binding constant, K_P for the water-soluble PDMAEMA statistical quaternary ammonium salts with sodium chloroacetate versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$



The data show that, as the degree of quaternisation with sodium chloroacetate is increased, the maximum magnitude of the dye-binding constant is reduced. These results agree well with those observed with PDMAEMA quaternised with methyl iodide.

7.2.5.6 Calculation of K_P for a series of statistically quaternised water-soluble PDMAEMA co-polymers (2.12) with n-bromomethyl phthalimide

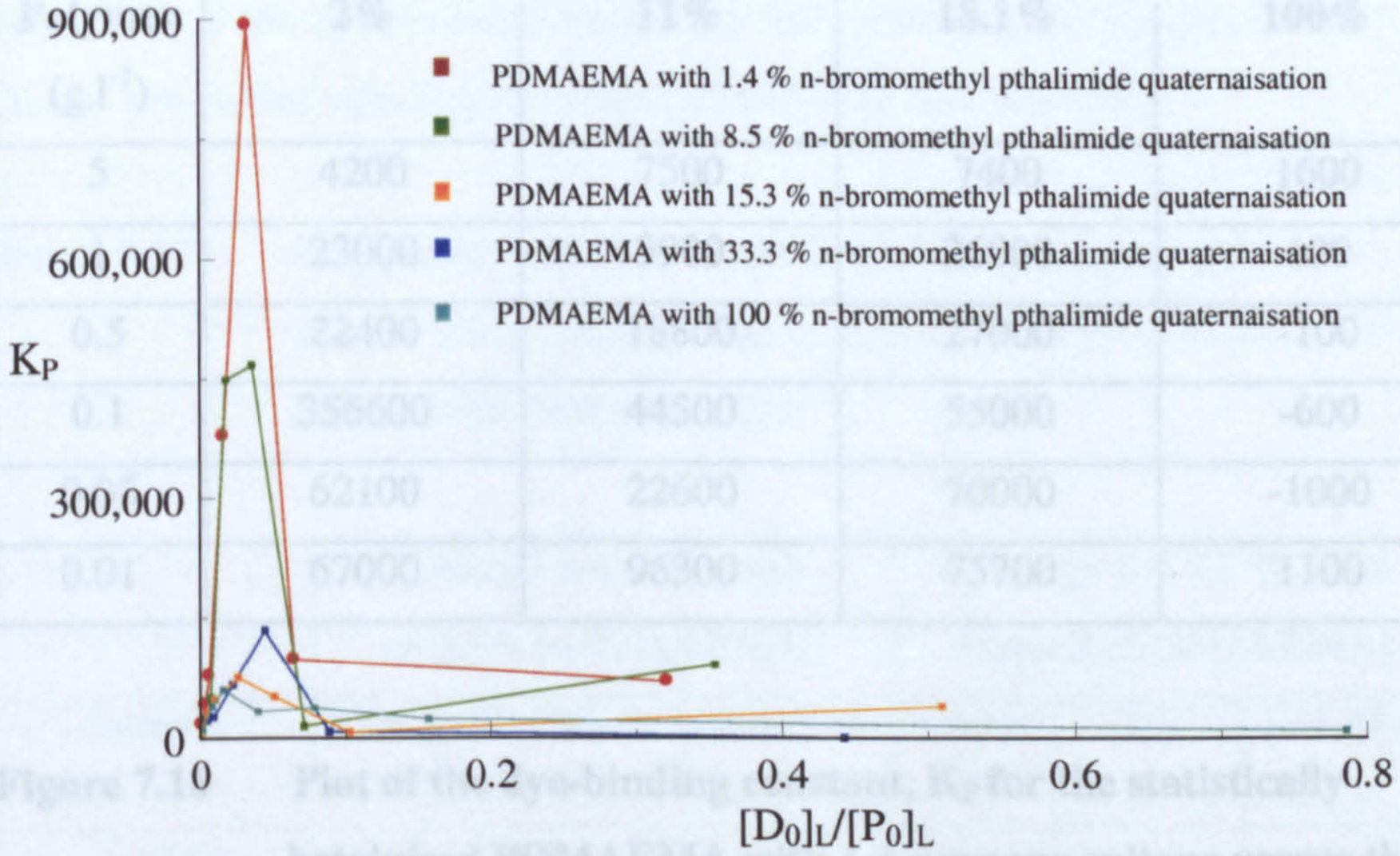
The dye-binding constant K_P was determined for a series of statistically quaternised water-soluble PDMAEMA co-polymers with n-bromomethyl phthalimide (**2.12**) (Mn ~ 22400) prepared by free radical polymerisation as described in Chapter 2.1.4.

Table 7.15 gives the dye-binding constants, K_P for a range of different water-soluble polymer PDMAEMA statistical quaternary ammonium salts with n-bromomethyl phthalimide.

Table 7.15 Calculated dye-binding constants for PDMAEMA statistical quaternary ammonium salts with n-bromomethyl phthalimide

	K_P PDMAEMA with n-bromomethyl phthalimide quaternisation				
Polymer ($g.l^{-1}$)	**1.4%**	**8.5%**	**15.3%**	**33.2%**	**100%**
5	17000	4600	10500	6600	8600
1	42100	23500	21500	36500	39200
0.5	77800	50600	25800	48200	59900
0.2	379100	448500	66700	75400	32200
0.1	892500	467200	134200	51700	37200
0.05	98300	14200	7400	6900	22500
0.01	69900	91100	-200	39300	8300

Figure 7.15 Plot of the dye-binding constant, K_P for the water-soluble PDMAEMA statistical quaternary ammonium salts with n-bromomethyl phthalimide versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$



The data show that, as the degree of quaternisation with n-bromomethyl phthalimide is increased, the maximum magnitude of the dye-binding constant is reduced.

7.2.5.7 Calculation of K_P for a series of statistically betainised water-soluble PDMAEMA co-polymers (2.13) with 1,3-propane sultone

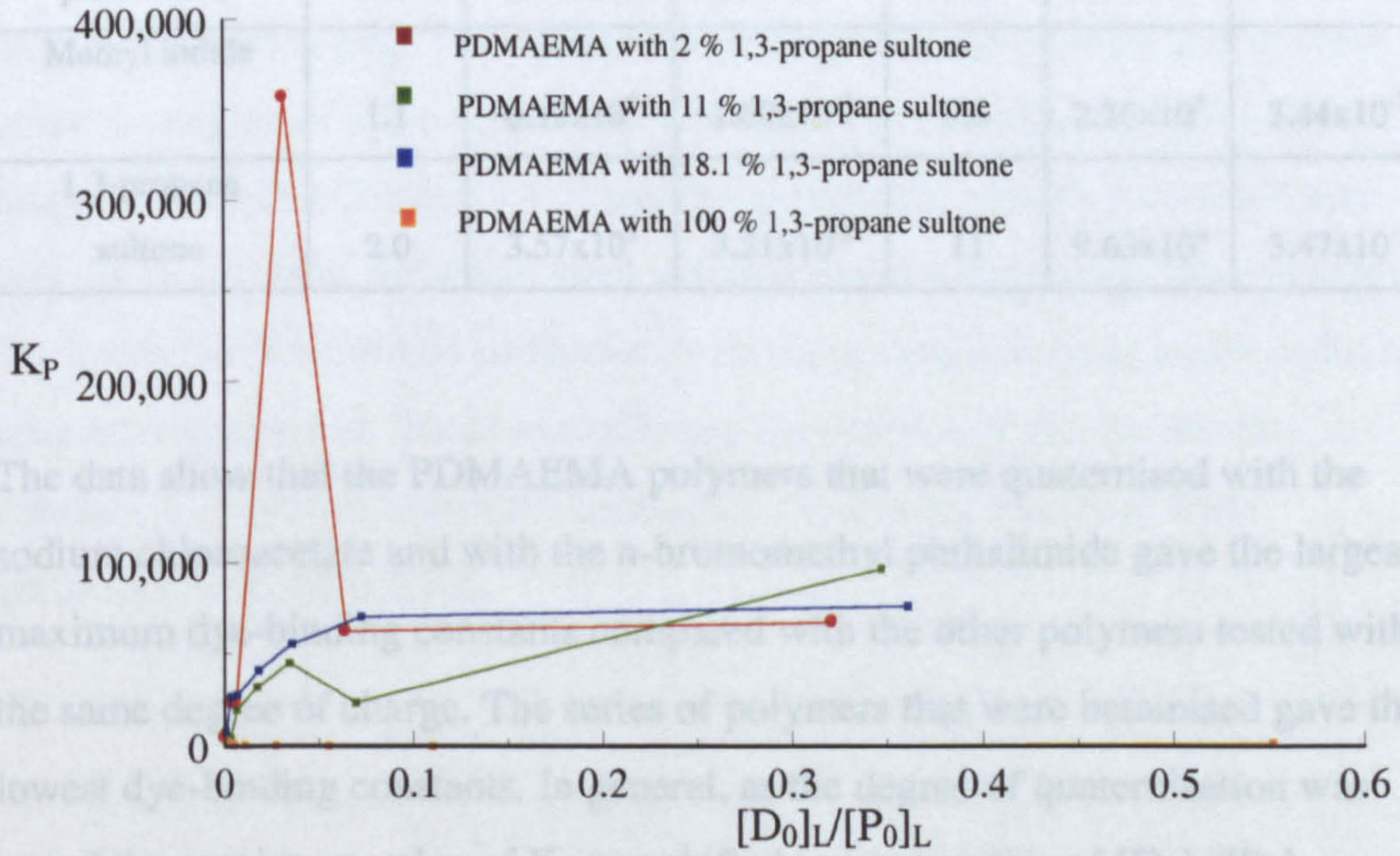
The dye-binding constant, K_P was determined for a series of statistically betainised water-soluble PDMAEMA co-polymers with 1,3-propane sultone (**2.13**) (Mn ~ 22400) prepared by free radical polymerisation as described in Chapter 2.1.5.

Table 7.16 gives the dye-binding constants, K_P for a range of different water-soluble PDMAEMA polymers statistically betainised with 1,3-propane sultone.

Table 7.16 Calculated dye-binding constants for PDMAEMA statistically betainised with 1,3-propane sultone

	K_P PDMAEMA with 1,3-propane sultone betainisation			
Polymer ($g.l^{-1}$)	**2%**	**11%**	**18.1%**	**100%**
5	4200	7500	7400	1600
1	23000	3900	26000	100
0.5	22400	18800	27000	-100
0.1	356600	44500	55000	-600
0.05	62100	22600	70000	-1000
0.01	67000	96300	75700	1100

Figure 7.16 Plot of the dye-binding constant, K_P for the statistically betainised PDMAEMA with 1,3-propane sultone versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$



The polymer containing 100 % betainisation precipitated at all concentrations from solution and therefore the data from this polymer should not be correlated

with the other tests. The data show that, as the degree of betainisation with 1,3-propane sultone is increased that, maximum magnitude of the dye-binding constant is reduced.

Table 7.17 gives a comparison of the change in the position and maximum magnitude of the dye binding constant for analogous polymer species where charge was added with respect to the [DMAEMA] concentration.

Table 7.17 Comparison of the change in K_P for analogous polymer species where charge was added with respect to the [DMAEMA] concentration

	Charge is 1-2 % with respect to [DMAEMA]			Charge is 7-11 % with respect to [DMAEMA]		
Sample	**Charge %**	**K_P**	**$[D_0]_L/[P_0]_L$**	**Charge %**	**K_P**	**$[D_0]_L/[P_0]_L$**
Sodium chloroacetate	1	$1.17x10^{6}$	$3.21x10^{-2}$	7	$2.61x10^{5}$	$3.26x10^{1}$
n-bromomethyl phthalimide	1.4	$8.93x10^{5}$	$3.21x10^{-2}$	8.5	$4.67x10^{5}$	$3.54x10^{-2}$
Methyl iodide	1.1	$6.12x10^{5}$	$1.60x10^{-2}$	9.6	$2.26x10^{5}$	$3.44x10^{-2}$
1,3-propane sultone	2.0	$3.57x10^{5}$	$3.21x10^{-2}$	11	$9.63x10^{4}$	$3.47x10^{-1}$

The data show that the PDMAEMA polymers that were quaternised with the sodium chloroacetate and with the n-bromomethyl phthalimide gave the largest maximum dye-binding constants compared with the other polymers tested with the same degree of charge. The series of polymers that were betainised gave the lowest dye-binding constants. In general, as the degree of quaternisation was raised the maximum value of K_P was shifted to lower ratios of $[D_0]_L/[P_0]_L$. When a degree of permanent charge is incorporated into the polymer then an increase in the coil extension of the polymer in solution occurs. The available binding site concentration of a polymer in an extended coil conformation is

closer to the theoretical concentration where all monomer units are considered to be available as binding sites than for the polymer in a closed coil conformation. The chain extension of the polymer that results from binding with dye is less pronounced when permanent charge is already present in the polymer species. A larger percentage of the total binding site concentration $[P_0]_L$ is available from the polymer that contains permanent charge due to the increased coil extension and therefore fewer binding sites become available when dye is added to the polymer species. As more permanent charge is incorporated into polymer then less dye is required to reach the maximum chain extension and therefore the maximum value of K_P and this is observed in the maximum value of K_P being shifted to lower ratios of $[D_0]_L/[P_0]_L$.

All polymers gave dye-binding constants that were up to several orders of magnitude greater than those determined for known anti-dye transfer agents, PVP K-25 ($K_P < 500$) and the literature value for PVP-co-PVI (**7.5**) ($K_P \sim$ 40000). The data from these studies is therefore contrary to the data obtained from the qualitative studies performed in Section 7.1.2 where PVP-co-PVI (**7.5**) gave a dramatic reduction in the degree of dye transfer to a white non-bleached cotton cloth from a dye in a surfactant solution. PDMAEMA and its quaternary salts all showed negligible reduction in the degree of dye transfer and in some cases the degree of dye transfer was increased. The difference between the qualitative studies (Section 7.1.2) and the quantitative studies performed here was the inclusion of surfactant stock solution in the simulated qualitative study. To determine the effect of surfactant on the static sorption study a new series of tests were performed. These tests allowed the analysis of the dye-binding constant K_P with true simulated laundering conditions, similar to those performed in Section 7.1.2.

7.2.5.8 Tests to determine whether surfactants interact with direct red 80 dye in aqueous solution

Before a dye in a surfactant solution can be analysed with a polymer for dye-binding it is first necessary to determine whether the dye interacts with the components of the surfactant stock solution. Each component of the surfactant was independently tested for its interaction with the dye. Each component was dissolved into a solution of the dye in deionised water to give the correct relative concentrations as those used in the surfactant stock solution outlined in Figure 7.0. The UV/Visible spectra for the dye solution and the solution containing each component were then analysed between 400 and 780 nm. The non-ionic surfactant was insoluble in a solution of dye in deionised water and therefore no tests were performed to study the interaction of non-ionic surfactant with Direct Red 80. Table 7.18 lists the surfactant components from each solution.

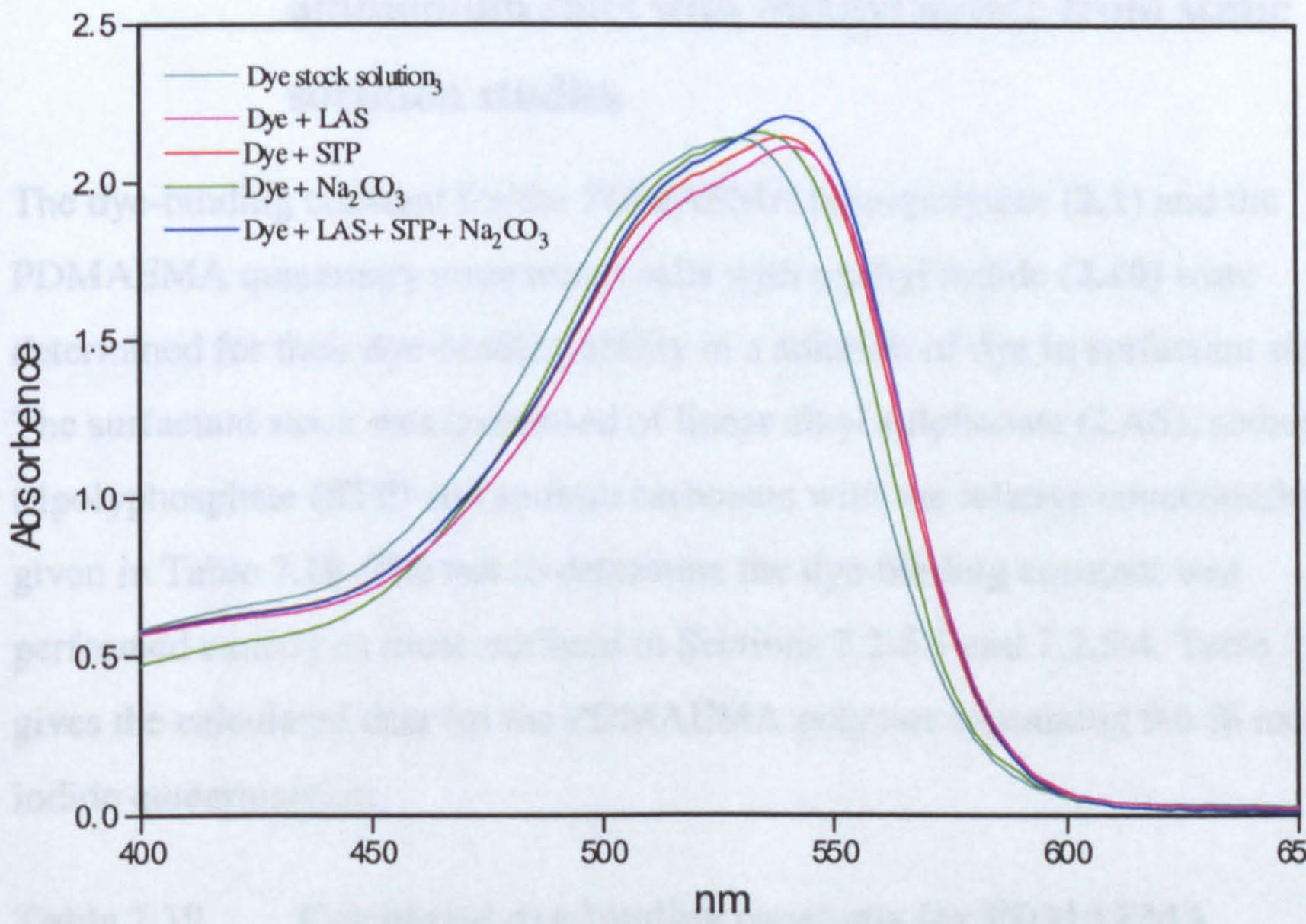
Table 7.18 Surfactant components analysed for their interaction with Direct Red 80

Sample	Structure	Concentration
Linear alkyl sulphonate (LAS) (Anionic surfactant)	**(7.0)**	1.6 gl^{-1}
Sodium tripolyphosphate (STP) (Anti-redeposition agent and metal extraction active)	**(7.2)**	1.2 gl^{-1}
Sodium Carbonate (Increase of ionic strength and pH)	**(7.3)**	0.4 gl^{-1}

A solution of each was prepared to give the desired concentration in a dye stock solution in deionised water where the dye concentration was determined by UV/Visible spectroscopy at 534 nm to be 2.01 $x10^{-5}$ mol l^{-1}. One other solution was prepared that contained all three components from the surfactant stock to determine whether there was any combined effect not observed by individual

analysis. The UV/visible spectra of each of these solutions were then determined and an overlay of these spectra with the initial dye-stock solution is given in Figure 7.17.

Figure 7.17 UV/Visible spectra for components of the surfactant in aqueous dye solution compared with the dye stock solution



The spectra show that the addition of sodium carbonate had virtually no effect on the visible spectrum of the dye in solution. The stock solutions containing sodium tripolyphosphate (STP) and the linear alkyl sulphonate (LAS) showed the evolution of a small shoulder peaks with a bathochromic shift to higher wavelength at 540 nm by 6 nm. The optical density of the band at 534 nm was shown to be invariant to the addition of the STP or LAS. The mixture that contained all three components from the surfactant stock also showed the evolution of a small shoulder at 540 nm. The evolution of the shoulder peaks in the spectra did not affect the overall absorption at 534 nm and therefore as far as possible it is determined that no binding interaction between the dye and the surfactant components occurs. The determination of the dye-binding constant K_P by static sorption in the presence of surfactant stock solution is therefore possible.

7.2.6 Dye-binding constants, K_P for water-soluble polymers in the presence of dye with anionic surfactant stock solution present

7.2.6.1 Tests to determine the dye-binding constants, K_P for PDMAEMA and PDMAEMA quaternary ammonium salts with methyl iodide from static sorption studies

The dye-binding constant for the PDMAEMA homopolymer (**2.1**) and the PDMAEMA quaternary ammonium salts with methyl iodide (**2.10**) were determined for their dye-binding ability in a solution of dye in surfactant stock. The surfactant stock was composed of linear alkyl sulphonate (LAS), sodium tripolyphosphate (STP) and sodium carbonate with the relative concentrations given in Table 7.18. The test to determine the dye-binding constant was performed exactly as those outlined in Sections 7.2.5.3 and 7.2.5.4. Table 7.19 gives the calculated data for the PDMAEMA polymer containing 9.6 % methyl iodide quaternisation.

Table 7.19 Calculated dye-binding constants for PDMAEMA quaternised with 9.6 % methyl iodide in surfactant

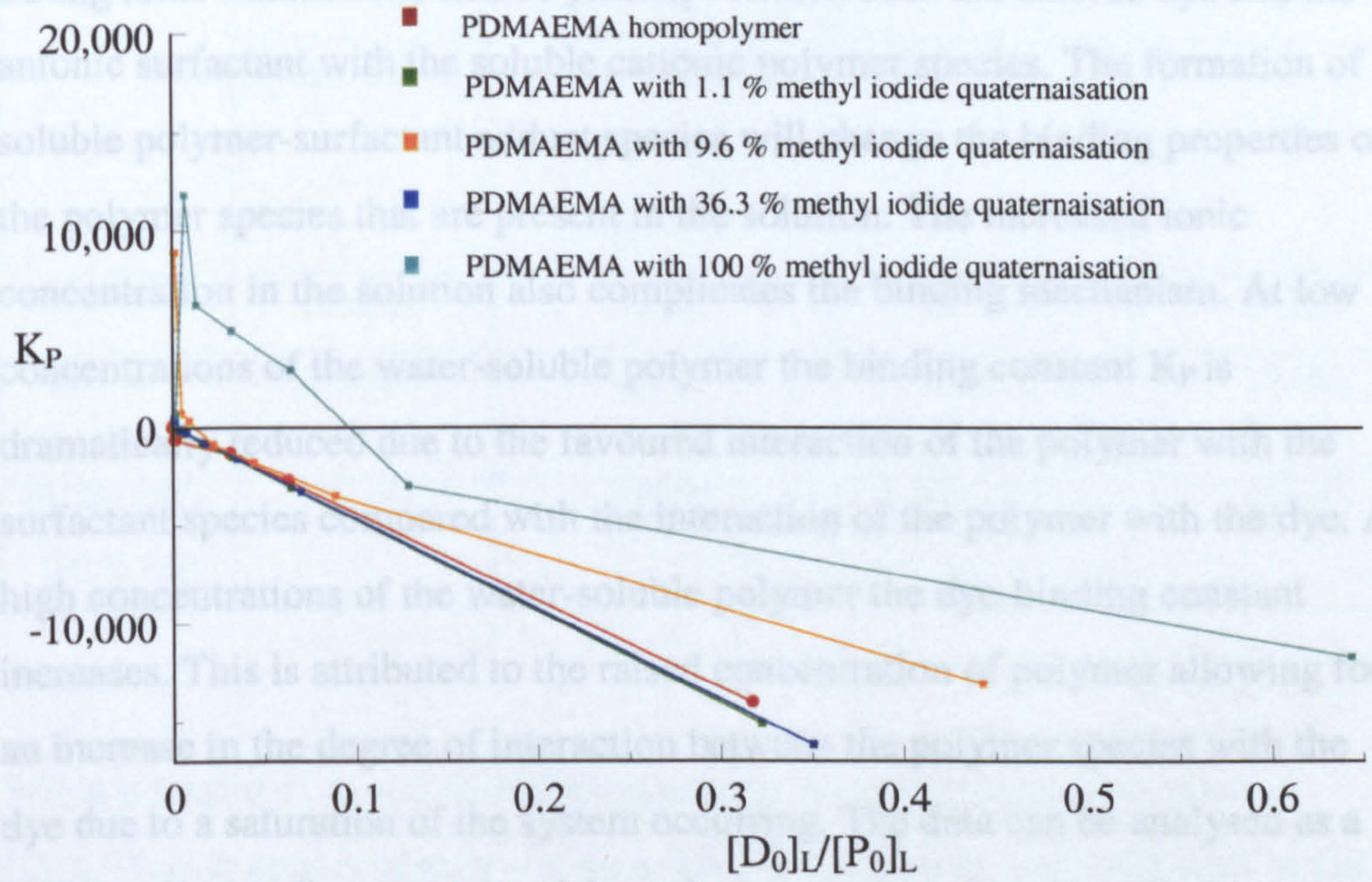
Polymer ($g.l^{-1}$)	**A_1** Absorption at 534 nm (dye with water soluble polymer)	**A_2** Absorption at 534 nm (dye with water soluble polymer and cross-linked polymer)	**K_P**
0	Dye stock solution, $[D_0]_L = 2.05 \times 10^{-5}$ mol l^{-1}		
5	2.2326	0.8607	400
1	2.0970	0.0260	-100
0.5	2.1421	0.0158	-300
0.2	1.9298	0.0101	-800
0.1	2.0160	0.0067	-1600
0.05	2.1074	0.0035	-3300
0.01	2.1377	0.0035	-16200

Table 7.20 gives the dye-binding constants, K_P for PDMAEMA and for the range of different water-soluble polymer PDMAEMA statistical quaternary ammonium salts with methyl iodide in surfactant stock.

Table 7.20 Calculated dye-binding constants for PDMAEMA and PDMAEMA statistical quaternary ammonium salts with methyl iodide in surfactant stock solution

	K_P PDMAEMA and PDMAEMA with methyl iodide quaternisation				
Polymer ($g.l^{-1}$)	**0%**	**1.1%**	**9.6%**	**36.3%**	**100%**
5	0	0	400	8900	600
1	-100	-200	-100	700	11800
0.5	-300	-300	-300	300	6200
0.2	-700	-800	-800	-900	4900
0.1	-1400	-1500	-1600	-1800	2900
0.05	-2800	-3100	-3300	-3500	-3000
0.01	-14100	-15100	-16200	-13100	-11700

Figure 7.18 Plot of the dye-binding constant, K_P for PDMAEMA and the PDMAEMA statistical quaternary ammonium salts with methyl iodide versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$



Little or no decrease in the absorption of the dye in the solution was detected after the addition of the soluble polymer. A large decrease in the concentration of the dye in solution was observed with the subsequent addition of the water-insoluble cross-linked polymer. Where the difference between these two concentrations is large the dye-binding constant K_P for the cross-linked polymer became negative. This is believed to result from the favoured interaction of the polymer with surfactant forming soluble adduct species. The formation of the soluble adduct gives a reduction in the concentration of available binding sites; this is not taken into consideration in the determination of K_P and results in a negative value for K_P. As the binding interaction of the polymer with anionic surfactant increases then a larger negative value of K_P is found.

The data shows that as a general rule, as the concentration of the water-soluble polymer is increased, the dye-binding constant K_P increases. As the degree of quaternisation in the polymer species is increased then the dye-binding constant K_P for the water soluble-polymer increases at high concentrations and decreases

at low concentrations. This trend in the data suggests that the concentration of the water-soluble polymer has a direct link with the magnitude of the dye-binding constant K_P.

Strong ionic interactions will be present between both the anionic dye and the anionic surfactant with the soluble cationic polymer species. The formation of soluble polymer-surfactant adduct species will change the binding properties of the polymer species that are present in the solution. The increased ionic concentration in the solution also complicates the binding mechanism. At low concentrations of the water-soluble polymer the binding constant K_P is dramatically reduced due to the favoured interaction of the polymer with the surfactant species compared with the interaction of the polymer with the dye. At high concentrations of the water-soluble polymer the dye-binding constant increases. This is attributed to the raised concentration of polymer allowing for an increase in the degree of interaction between the polymer species with the dye due to a saturation of the system occurring. The data can be analysed as a realistic dye-binding constant of the polymer species when the anionic surfactant is present. A comparison of these data with those obtained in the absence of surfactant shows that the dye-binding ability of the polymer is severely affected by the addition of the surfactant stock to the wash procedure.

A comparison of how these polymers performed during the qualitative tests outlined in Section 7.1.2 when the calculation of $[D_0]_L/[P_0]_L$ is known. For each experiment in Section 7.1.2 polymer (0.0435 $g.l^{-1}$) was added to a solution of dye ($1x10^{-1}$ $mol.l^{-1}$) in surfactant stock solution. The value of $[D_0]_L/[P_0]_L$ has been calculated for some of the test polymers that were analysed and these data are given in Table 7.21.

Table 7.21 Comparison of the degree of dye-transfer inhibition between qualitative and quantitative studies for PDMAEMA polymers in surfactant solution

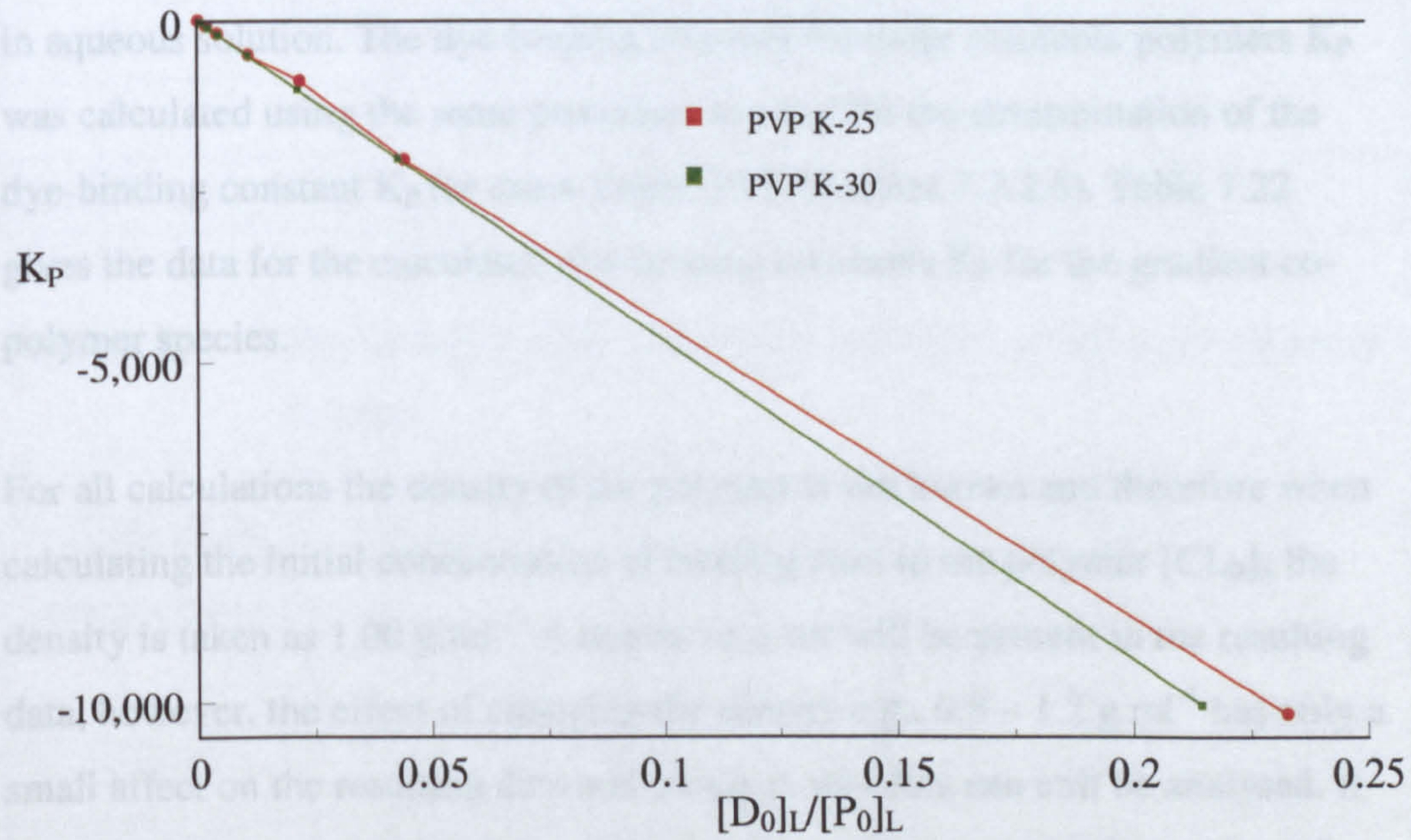
Polymer	Qualitative Study		Quantitative Study	
	$[D_0]_L/[P_0]_L$	Dye transfer δ (reflectance at 534nm)	$[D_0]_L/[P_0]_L$	K_P
PDMAEMA	0.3614	43.51	0.3192	- 14100
PDMAEMA 36.3 % MeI	0.4340	40.12	0.4426	- 13100
PDMAEMA 100 % MeI	0.6888	30.88	0.6437	- 11700

When the ratio of dye to dye binding sites in the water soluble polymer $[D_0]_L/[P_0]_L$ is approximately the same for the qualitative determination of the dye pick up onto a cotton cloth as for the quantitative determination of K_P then a comparison for trends in the data can be made. For the qualitative study the degree of dye transfer is inhibited as the degree of quaternisation is increased. This is observed as a decrease in the delta reflectance of the cotton cloth at 534 nm after washing. The quantitative determination of K_P in a surfactant solution shows that, as the degree of quaternisation is increased, the dye-binding constant K_P increases. Although the data for K_P are all negative they become less negative as the degree of quaternisation is increased. This trend in the data agrees well with the observed reduction in dye transfer from the qualitative study. The negative value of K_P is indicative of the complex binding behaviour of the polymer with the dye and with surfactant.

7.2.6.2 Tests to determine the dye-binding constants, K_P for water-soluble poly(N-vinyl pyrrolidone)s PVP K-25 and PVP K-30 from static sorption studies

The dye-binding constants for the water-soluble poly(N-vinyl pyrrolidone) polymers PVP K-25 and PVP K-30 were determined. Figure 7.19 gives a plot of the dye-binding constant K_P versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$ for the poly(N-vinyl pyrrolidone) polymers.

Figure 7.19 Plot of the dye-binding constant, K_P for PVP K-25 and PVP K-30 versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$



The data show that, as the concentration of the polymer increases, the dye-binding constant increases. Poly(N-vinyl pyrrolidone) polymers exhibit similar data for their dye-binding behaviour as shown by PDMAEMA. No direct comparison can be made between the magnitude of K_P determined for PVP in comparison to PDMAEMA due to the unknown partitioning behaviour of the two respective polymers with dye and surfactant.

7.2.7 Dye-binding constants, K_S for insoluble gradient co-polymers prepared from Atom Transfer Polymerisation

The dye-binding constants K_P for a series of gradient co-polymers were investigated for dye in deionised water and dye in surfactant solutions. These tests were performed in order to understand whether by controlling the architecture of the polymer species, such that all of the permanent charge was located at one end of the polymer chain, would alter the dye-binding behaviour of the polymer species. The species are all PDMAEMA-co-PDEAEMA gradient co-polymers where selective quaternisation of the PDMAEMA residue has been performed through reaction with methyl iodide.

The gradient co-polymers where no quaternisation was present were insoluble in aqueous solution. The dye-binding constant for these insoluble polymers K_P was calculated using the same procedure as used for the determination of the dye-binding constant K_P for cross-linked PVP (Section 7.2.2.6). Table 7.22 gives the data for the calculated dye-binding constants K_P for the gradient co-polymer species.

For all calculations the density of the polymer is not known and therefore when calculating the initial concentration of binding sites in the polymer $[CL_0]_S$ the density is taken as 1.00 $g.ml^{-1}$. A degree of error will be present in the resulting data, however, the effect of changing the density e.g., 0.8 – 1.2 g ml^{-1} has only a small affect on the resulting data and trends in this data can still be analysed. It should also be noted that for the determination of the concentration of bound sites in the solid polymer compartment $[CL.D]_S$ that the amount of dye that is present in the polymer phase that is not bound $([D]_L)_S$ is given as zero. This assumption is made on the grounds that a linear system is present in comparison to the cross-linked system examined for PVP-CL where the dye can enter the polymer network. Therefore Equation 7.11 becomes:

$$[CL.D]_S = \frac{1}{\varphi}([D_o]_L - [D]_L) \qquad (7.28)$$

Table 7.22 Calculation of the initial concentration of binding sites $[CL_0]_S$ for the insoluble polymer species

[PDMAEMA]:[PDEAEMA] gradient co-polymer	Density ($g.ml^{-1}$)	RMM of repeat unit ($g.mol^{-1}$)	$[CL_0]_S$ ($mol.l^{-1}$)
[63]:[37]	1.00	167.32	5.98
[35.7]:[64.3]	1.00	174.05	5.75
[10.3]:[89.7]	1.00	180.22	5.55

Table 7.23 Calculation of the phase ratio, φ for the gradient co-polymers for the static sorption studies

Polymer ($g.l^{-1}$)	Polymer (g)	Volume of polymer (ml)	$\varphi = \frac{\text{Volume of polymer}}{\text{Volume of liquid}}$
1	0.025	0.025	0.0005
5	0.125	0.125	0.0025
10	0.25	0.25	0.005

Table 7.24 Dye binding constants K_P for insoluble gradient co-polymer species

[PDMAEMA]:[PDEAEMA]	Polymer (g)	φ $x10^{-3}$	$[D]_L$ ($moll^{-1}$) $x10^{-5}$	$[CL.D]_S$ ($moll^{-1}$) $x10^{-3}$	K_S
[63]:[37]	1	0.5	1.88	2.443	21.8
[63]:[37]	5	2.5	1.85	4.745	5.4
[63]:[37]	10	5	1.79	6.477	4.0
[35.7]:[64.3]	1	0.5	1.76	0.599	46.9
[35.7]:[64.3]	5	2.5	1.74	1.027	10.3
[35.7]:[64.3]	10	5	1.65	1.726	7.5
[10.3]:[89.7]	1	0.5	1.67	0.426	69.7
[10.3]:[89.7]	5	2.5	1.57	0.705	19.8
[10.3]:[89.7]	10	5	1.51	0.987	11.8

The data show that the dye-binding constant K_S for the insoluble gradient co-polymer species varies as the concentration of the polymer is changed compared with the dye concentration. The dye-binding constant was shown to decrease as the concentration of polymer was increased in the system; this is unexpected for a heterogeneous system. For cross-linked poly(N-vinyl pyrrolidone) the dye-binding constant remains constant as the relative polymer concentration is changed with respect to dye. The variation observed here might be in part due to the linear nature of the polymer species opposed to the cross-linked nature of the PVP system. A degree of solvation of the polymer species may occur, resulting in concentration dependent shifts in the value of K_S. As the ratio of [DEAEMA] is increased in the gradient co-polymer then the relative dye-binding ability is shown to increase at all concentrations tested. This suggests that DEAEMA residues are stronger dye-binding agents than the DMAEMA residues, possibly due to the more nucleophilic nature of DEAEMA in comparison to DMAEMA and changes in the pH of the two polymers.

7.2.8 Dye-binding constants, K_P for partially quaternised gradient co-polymers

All gradient co-polymer species that had been quaternised to known degrees were soluble in deionised water and surfactant solution. Table 7.25 lists the polymers that have been analysed in terms of their monomer composition to allow a comparison to be made with the dye-binding data from the statistical PDMAEMA quaternary salts. The monomer composition is calculated based on ideal selective quaternisation of the PDMAEMA block.

Table 7.25 Gradient co-polymer composition for dye-binding tests

[PDMAEMA]:[PDEAEMA] gradient co-polymer	% quaternisation with respect to [PDMAEMA]	% quaternisation with respect to [PDMAEMA]+ [PDEAEMA]
[63]:[37]	100	63
[63]:[37]	60	37.8
[63]:[37]	20	12.6
[35.7]:[64.3]	100	35.7
[35.7]:[64.3]	60	21.4
[35.7]:[64.3]	20	7.2
[10.3]:[89.7]	100	10.3
[10.3]:[89.7]	60	6.2
[10.3]:[89.7]	20	2.0

The dye-binding constant for each polymer was determined by static sorption in both deionised water and in surfactant solution. The tests that were performed to determine the dye-binding constant for the polymer in deionised water used the method outlined in Section 7.2.5.1 for PVP K-25. The tests that were performed to determine the dye-binding constant for the polymer in the presence of surfactant solution used the method outlined in Section 7.2.6.

7.2.8.1 Dye-binding constants, K_P for gradient co-polymers where quaternisation is 20, 60 and 100 % with respect to [DMAEMA] in deionised water

The dye-binding constants K_P were determined for the series of gradient co-polymers where quaternisation was added to give 20, 40 and 100 % quaternisation with respect to [DMAEMA].

Figure 7.20 **Plot of the dye-binding constant, K_P for the gradient co-polymers where quaternisation is 20 % with respect to [DMAEMA] versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$ in deionised water**

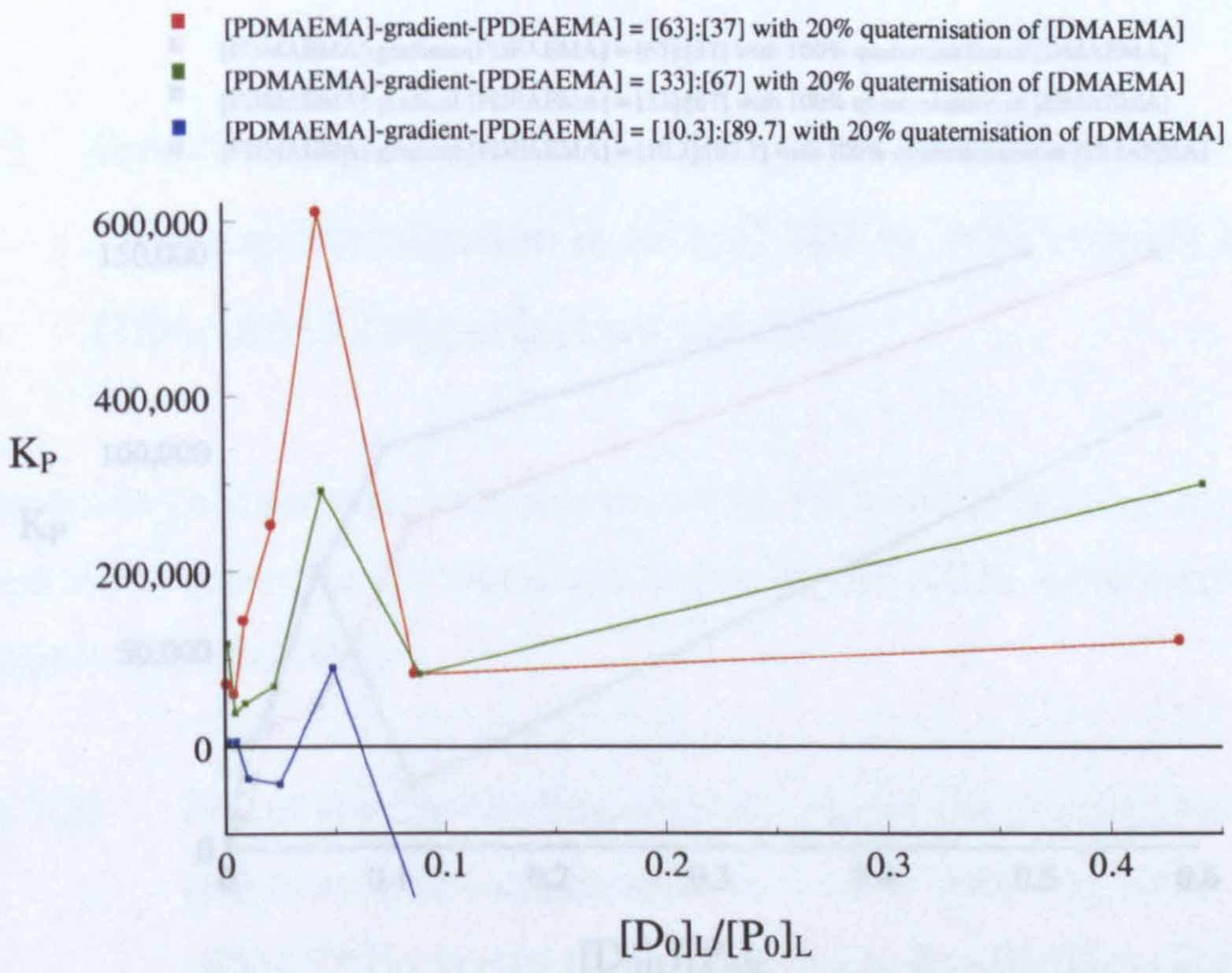


Figure 7.21 **Plot of the dye-binding constant, K_P for the gradient co-polymers where quaternisation is 60 % with respect to [DMAEMA] versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$ in deionised water**

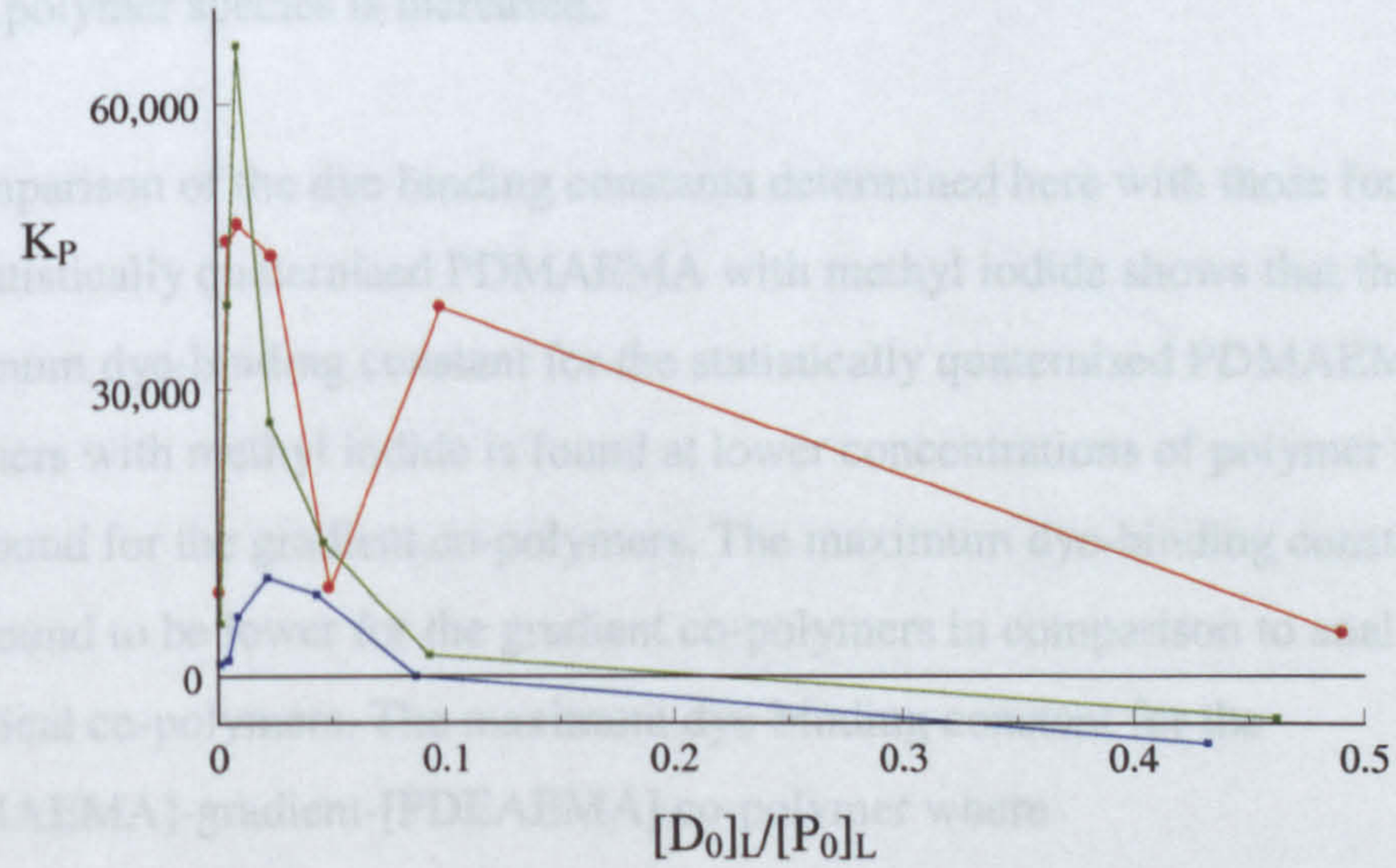
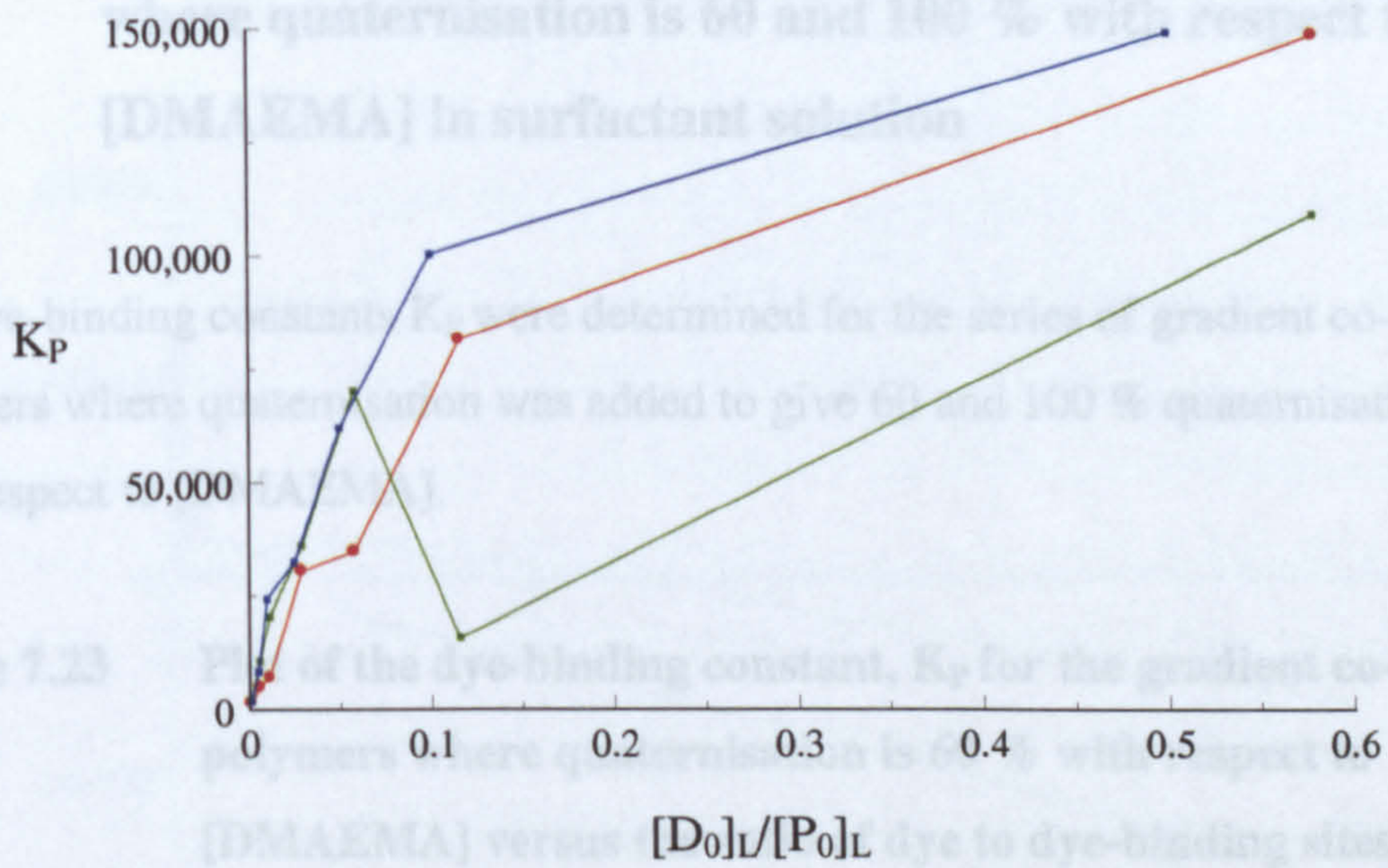


Figure 7.22 Plot of the dye-binding constant, K_P for the gradient co-polymers where quaternisation is 100 % with respect to [DMAEMA] versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$ in deionised water



The plots of the dye-binding constant versus the ratio of dye to available dye binding sites in the polymer $[D_0]_L/[P_0]_L$ for the gradient co-polymers show that at all degrees of quaternisation, as the relative concentration of [DEAEMA] is increased in the polymer the maximum dye-binding constant of the polymer is decreased. The effect becomes less pronounced as the degree of quaternisation in the polymer species is increased.

A comparison of the dye binding constants determined here with those found for statistically quaternised PDMAEMA with methyl iodide shows that the maximum dye-binding constant for the statistically quaternised PDMAEMA polymers with methyl iodide is found at lower concentrations of polymer than that found for the gradient co-polymers. The maximum dye-binding constant is also found to be lower for the gradient co-polymers in comparison to analogous statistical co-polymers. The maximum dye-binding constant for the [PDMAEMA]-gradient-[PDEAEMA] co-polymer where

[DMAEMA:[DEAEMA] was [63]:[37] with 37.8 % selective quaternisation gave K_P ~ 58000 at $[D_0]_L/[P_0]_L$ ~ 0.01, in comparison the PDMAEMA statistical co-polymer with methyl iodide where quaternisation was 36.6 % gave K_P ~ 153000 at $[D_0]_L/[P_0]_L$ ~ 0.5.

7.2.8.2 Dye-binding constants, K_P for gradient co-polymers where quaternisation is 60 and 100 % with respect to [DMAEMA] in surfactant solution

The dye-binding constants K_P were determined for the series of gradient co-polymers where quaternisation was added to give 60 and 100 % quaternisation with respect to [DMAEMA].

Figure 7.23 Plot of the dye-binding constant, K_P for the gradient co-polymers where quaternisation is 60 % with respect to [DMAEMA] versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$ in surfactant solution

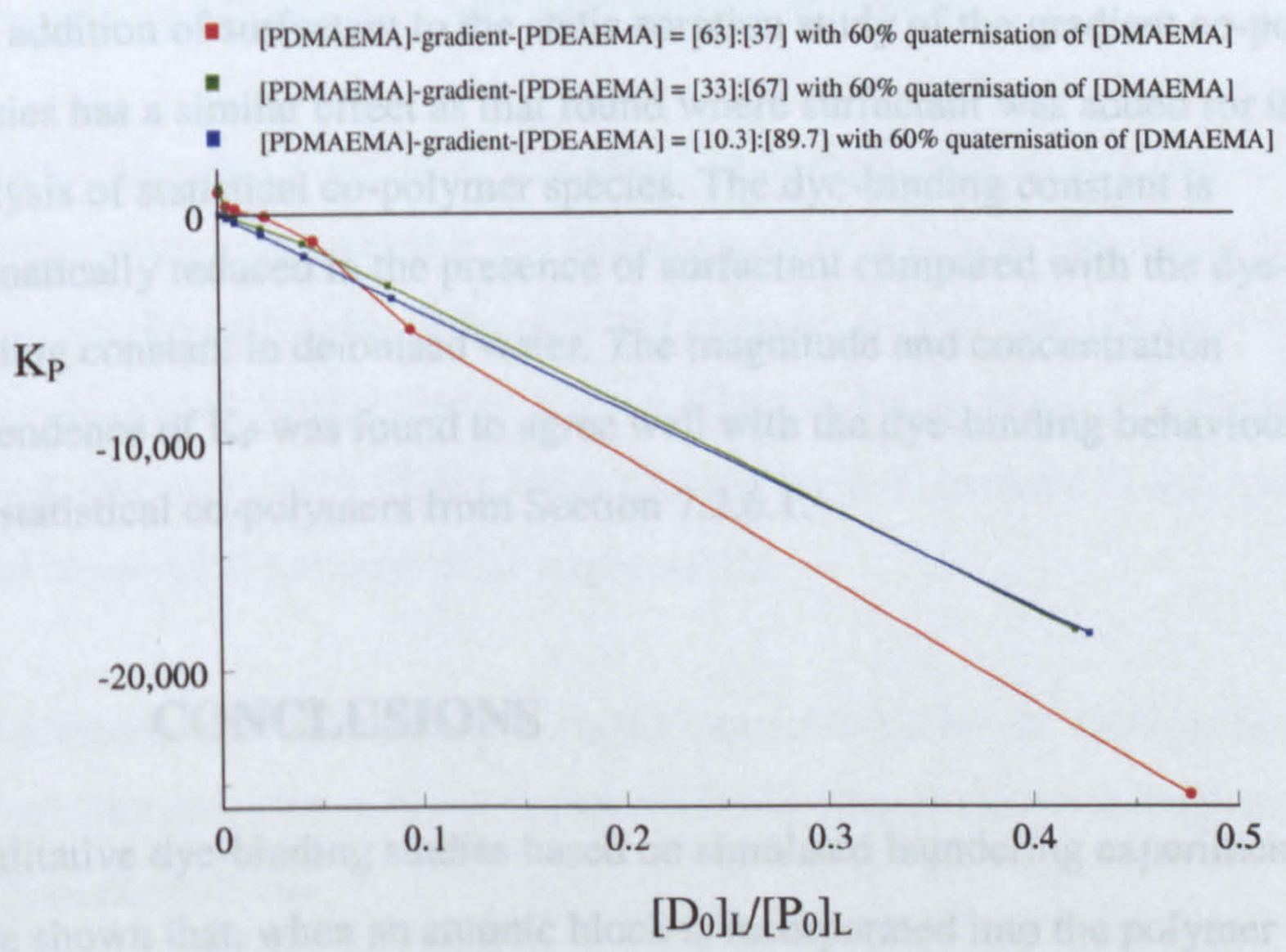
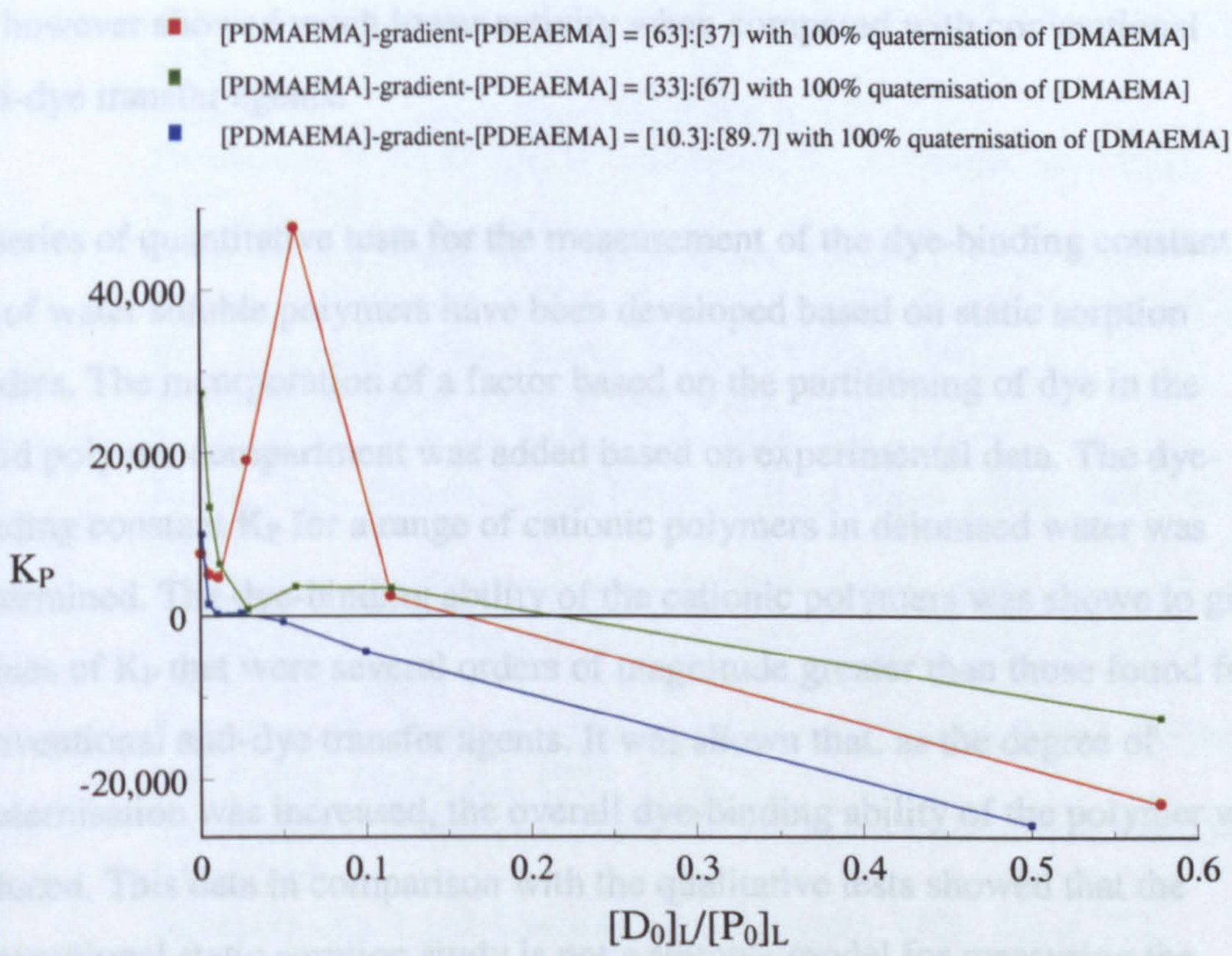


Figure 7.24 Plot of the dye-binding constant, K_P for the gradient co-polymers where quaternisation is 100 % with respect to [DMAEMA] versus the ratio of dye to dye-binding sites in the water-soluble polymer, $[D_0]_L/[P_0]_L$ in surfactant solution



The addition of surfactant to the static sorption study of the gradient co-polymer species has a similar effect as that found where surfactant was added for the analysis of statistical co-polymer species. The dye-binding constant is dramatically reduced in the presence of surfactant compared with the dye-binding constant in deionised water. The magnitude and concentration dependence of K_P was found to agree well with the dye-binding behaviour of the statistical co-polymers from Section 7.2.6.1.

7.3 CONCLUSIONS

Qualitative dye-binding studies based on simulated laundering experiments have shown that, when an anionic block is incorporated into the polymer species, a reduction in the overall dye-binding ability occurs. These results agree well with those reported in the literature for the analysis of statistical co-

polymers containing acrylic acid and poly(N-vinyl pyrrolidone). This reduction in the overall dye-binding ability of the polymer is due to electrostatic repulsion between the charged polymer with the anionic dye. Inclusion of a statistical degree of cationic charge into the PDMAEMA polymer gave a noticeable increase in the degree of dye-transfer inhibition obtained. The cationic polymers all however showed much lower activity when compared with conventional anti-dye transfer agents.

A series of quantitative tests for the measurement of the dye-binding constant K_P of water soluble polymers have been developed based on static sorption studies. The incorporation of a factor based on the partitioning of dye in the solid polymer compartment was added based on experimental data. The dye-binding constant K_P for a range of cationic polymers in deionised water was determined. The dye-binding ability of the cationic polymers was shown to give values of K_P that were several orders of magnitude greater than those found for conventional anti-dye transfer agents. It was shown that, as the degree of quaternisation was increased, the overall dye-binding ability of the polymer was reduced. This data in comparison with the qualitative tests showed that the conventional static sorption study is not a suitable model for measuring the degree of dye-transfer for a simulated laundering system.

The static sorption experiment was modified so that measurement of the dye-binding constant was possible in a surfactant stock solution. The results from these tests showed trends in the data that agreed well with that obtained from the qualitative simulated laundering experiments. The inclusion of permanent cationic charge into the PDMAEMA polymer gave an increase in the value of K_P as observed in the qualitative experiments.

No increase in the dye-binding constant was observed for the changes made in the polymer architecture from statistical distribution of charge through to a gradient distribution.

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Chapter 8

CONCLUSIONS

AND

FUTURE WORK

Go
some
distance
away because
the work appears
smaller and more of it
can be taken in at a glance
and a lack of harmony or proportion ***is rapidly seen***
Leonardo da Vinci

8.0 CONCLUSIONS

The dye-binding ability, K_P of a series of novel water-soluble synthetic polymers were determined using an adapted version of the static sorption technique used by Runge *et al* with cross-linked poly(N-vinyl pyrrolidone) PVP-CL [1]. A function based on the experimentally determined partitioning of dye in the solid polymer compartment of the cross-linked poly(N-vinyl pyrrolidone) PVP-CL was introduced and data using this new method were found to have improved reproducibility in comparison with previous studies [1]. A novel static sorption technique to determine the dye-binding constant, K_P of a water-soluble polymer with dye in the presence of anionic surfactant stock solution was developed.

PDMAEMA homopolymer was synthesised from radical polymerisation and the product polymer was statistically quaternised. Catalytic chain-transfer (CCT) polymerisation with CoBF of DMAEMA and MAA was used to prepare low molecular weight macromonomer species. The DMAEMA macromonomer species were subsequently used to prepare block co-polymers with MAA. Atom transfer polymerisation (ATP) of DMAEMA was successfully performed. The preparation of block co-polymers that contained both amine functional monomers in the A and B blocks from ATP were shown to produce homopolymer impurity. The loss of control from these block co-polymer syntheses is thought to result from the elimination of the bromine end group from the PDMAEMA macro-initiator. Cationic gradient co-polymer species were prepared from atom transfer polymerisation (ATP) to yield PDMAEMA-gradient-PDEAEMA co-polymers. These gradient co-polymer species were then selectively quaternised at the DMAEMA residue. Reversible addition-fragmentation transfer (RAFT) polymerisation was examined as a possible method for the preparation of PDMAEMA-block-PDMAEMA.MeI co-polymers. Controlled RAFT polymerisation of DMAEMA was shown proceed with a very low rate of polymerisation and therefore no further work was performed.

It has been shown that the dye-binding ability of Direct Red 80 with PDMAEMA homopolymer in deionised water is several orders of magnitude greater than that with the commercial anti-dye transfer agent PVP K-25. The larger dye-binding ability of PDMAEMA in comparison to PVP is explained in terms of its stronger cationic attraction with the anionic azo-dye. The dye-binding ability of Direct Red 80 with PDMAEMA homopolymer in an anionic surfactant solution gave a large reduction in the dye-binding constant with the anionic dye. Where an electrostatic attraction between the polymer and the surfactant occurs then this lead to the formation of soluble adduct species. The formation of the soluble adduct gave a reduction in the concentration of the available dye-binding sites in the polymer; that reduction was not taken into consideration in the determination of K_P and results in a negative value. As the binding interaction of the polymer with anionic surfactant increased then a larger negative value of K_P was found. The dye-binding ability of a water-soluble PDMAEMA homopolymer in deionised water decreased as the degree of incorporation of statistical quaternary charge was increased. This was attributed to the increased electrostatic repulsion of the polymer chain with the anionic dye. No increase in the dye-binding constant was found in comparing a statistical distribution of charge to a gradient distribution in either deionised water or anionic surfactant stock solution.

The incorporation of permanent anionic and cationic charge into a cationic polymer has been shown to result in a reduction in the dye-binding ability of the polymer species with anionic azo-dyes. The variation in the dye-binding constant of a cationic water-soluble polymer with varying degrees of permanent charge in deionised water is reversed for data obtained from surfactant stock solution. The data from surfactant stock solution agree well with those from qualitative simulated laundering experiments and therefore future tests to evaluate the dye-binding ability of water-soluble polymers should be analysed in terms of their performance in a simulated wash solution containing surfactant stock solution. PDMAEMA is more cationic than PVP and has a higher dye-binding constant in deionised water. PDMAEMA has a larger electrostatic interaction with anionic surfactant and therefore in simulated studies PDMAEMA has a lower dye-binding constant in comparison to PVP.

8.1 FUTURE WORK

A quantitative method to determine the degree of interaction of surfactant with a water-soluble polymer is required. The calculation of the dye-binding constant for the water-soluble polymer where the reduction in the available binding site concentration of the polymer due to interaction with surfactant is known will allow a comparison to be drawn between different cationic polymers in simulated washing conditions.

PVP and PVP-co-PVI both represent commercial polymers that contain cationic functionality that affords dye-binding behaviour together with negligible interaction with anionic surfactant. The incorporation of neutral hydrophilic functionality into a cationic polymer should be investigated to determine whether improved solubility of the dye-polymer adducts at high dye concentrations could be obtained without the incorporation of charge. New polymers should be investigated that are more cationic than PVP but that do not interact with anionic surfactant.

8.2 REFERENCES

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Chapter 9

EXPERIMENTAL SECTION

If you can dream it,

You can do it.

Walt Disney

9.0 GENERAL PROCEDURES

All polymerisation reactions were performed using standard Schlenk line apparatus under an atmosphere of dry nitrogen. Unless otherwise stated all polymerisation reactions were performed in Schlenk reaction tubes fitted with rubber septa. Chain transfer constants were determined using closed ampoules fitted with Rotorflow vacuum taps. All reagents were used as received unless otherwise stated. All monomers and solvents were degassed by purging with dry nitrogen for at least 2 hours or by using freeze/pump/thawing cycles. All liquid transfers were made with syringe. Yields of polymerisation were determined by drying a known amount of reaction solution to a constant weight in a vacuum oven maintained at 80 °C.

9.1 ANALYSIS

9.1.1 Molecular Weight Analysis

Polymer molecular weight was obtained from Gel Permeation Chromatography (GPC) using a Polymer Laboratories modular GPC system. Samples that were soluble in organic media were analysed using THF as an eluent at 1 ml min^{-1} with toluene (0.2 vol %) as an internal standard and flow marker in each sample. High molecular weight samples were analysed using a system equipped with two PL gel 5 μm mixed-C columns (300 x 7.5 mm) and one PL gel guard 5 μm column (50 x 7.5 mm). Low molecular weight samples were analysed using a system equipped with one PL gel 5 μm mixed-C column (300 x 7.5 mm) and one PL gel guard 5 μm column (50 x 7.5 mm). Both systems were equipped with a differential refractometer and calibrated with Polymer Laboratories PMMA standards from 200-1577000 Da.

Samples that were only soluble in aqueous media were analysed using pure deionised water buffered with 0.5 M NaCl and TRIZMA base at pH 6.7 as an eluent at 0.5 ml min^{-1} with acetone (0.1 vol %) as an internal standard and flow

marker in each sample. All samples were analysed with Toso Haas neutral hydrophobic stationary phase using a system equipped with two Toso Haas GMPW columns (300 x 7.5 mm) and a Toso Haas PWH guard column (50 x 7.5 mm). The system was equipped with a differential refractometer and calibrated with Polymer Laboratories PEG standards from 300-600000 Da.

9.1.2 NMR analysis

^{1}H NMR was carried out at 250.127 or 300.132 MHz. ^{1}H in TCE at 373 K, using Bruker ACF 250 MHz spectrometer or Bruker 300 MHz digital spectrometer. Quantitative ^{1}H NMR analysis of polymeric samples was gated so as to remove NOE with a relaxation delay of 30 seconds.

9.1.3 Infra-red spectrometry

All samples were analysed using a Bruker Vector 22 spectrometer equipped with a golden gate single reflection square diamond (2 x 2 mm) ATR PN 10500 from Graseby Specac. All liquid phase samples were analysed as pure liquids. Solid samples were analysed in CH_2Cl_2 as a solvent or as a fine dispersed powder.

9.1.4 Ultra-violet/visible spectroscopy

All UV/visible spectra were recorded using a JASCO V-570 spectrophotometer. Aqueous samples were analysed at 35 °C in polystyrene curvettes with a 1 cm path length. Organic soluble samples were analysed at 35 °C in quartz curvettes with a 1 cm path length.

9.2 REAGENTS AND SOURCES

- Cobalt (II) acetate, Copper (I) bromide, boron trifluoride etherate, MMA, BzMA, BzA, DMAEMA, DEAEMA, DMAEMA.HCl, MAA, AA, α-methyl styrene, n-pentyl amine, Sulfur, Benzyl chloride, Sodium methoxide (20 weight %), sodium hydroxide, carbon tetrachloride, methyl iodide, 1,3-propane sultone, n-bromomethyl pthalimide, chloroacetic acid, direct red 80,

THF, ethanol, methanol, toluene, dichloromethane, carbon tetrachloride, dichlorobenzene, (Aldrich)

- Dimethyl glyoxime (Lancaster)
- AIBN, HCl (BDH)
- CVA, ADMIBA.HCl (WAKO)
- Ethyl-2-bromoisobutyrate, Pyridine-2-carboxaldehyde (Avocardo)

9.3 SYNTHETIC EXPERIMENTAL PROCEDURES

9.3.1 Free-Radical Polymerisation

Monomer and initiator were dissolved into toluene. The reaction mixture was heated to 70 °C for 72 hours, after which time the reaction was cooled to 0 °C in an ice bath to terminate polymerisation and opened to air. Each reaction was performed with 35 weight % solids in toluene solution at 70 °C. All reactions were initiated with AIBN. The amount of initiator was varied to control the final degree of polymerisation of the product polymer.

9.3.2 Quaternisation of PDMAEMA homopolymer

Quaternisation of PDMAEMA homopolymer species was performed with three different alkyl halides (methyl iodide, n-bromomethyl pthalimide and chloroacetic acid sodium salt). For quaternisation with methyl iodide and n-bromomethyl pthalimide polymer was dissolved to give a 10 weight % solution in THF in a round bottom flask. For quaternisation with chloroacetic acid sodium salt then polymer was dissolved to give a 10 weight % solution in 50:50 water:methanol in a round bottom flask. Alkyl halide was added accurately to each solution and the reaction was stirred at 25 °C for 24 hours [1,2]. For reactions performed in THF products containing a high degree of quaternisation (>50%) precipitated during reaction. The quaternised product was recovered by the evaporation at reduced pressure from the solvent. The degree of quaternisation was determined by quantitative ^{1}H NMR analysis in D_2O. Products containing more than 50 % quaternisation were further purified by Soxhlet extraction with THF to remove unreacted alkyl halide.

9.3.3 Betainisation of PDMAEMA homopolymer

Betainisation of PDMAEMA homopolymer species was performed with 1,3-propane sultone. For each quaternisation reaction a 10 % solution of polymer was prepared into THF. 1,3-propane sultone was added to the solution and the reaction was stirred at 25 °C for 48 hours. The products containing a high degree of betainisation (>50%) precipitated from solution during reaction. The betainised product was recovered by evaporation under reduced pressure. The degree of betainisation was determined by quantitative ^{1}H NMR analysis in D_2O. The product that contained more than 50 % betainisation was further purified by Soxhlet extraction with THF to remove unreacted 1,3-propane sultone [3].

9.3.4 Catalytic Chain-Transfer (CCT) Polymerisation

9.3.4.1 Preparation of CoBF

CoBF was prepared by a modified method of Bakac and Espenson [4,5]. Cobalt (II) acetate tetrahydrate (8.21 g) was vacuum dried for 48 hours to give cobalt (II) diacetate as a dark red powder. Dimethylglyoximate (10 g) and dry cobalt (II) diacetate (8.21 g) were dissolved into 200 mL of dry and degassed ethyl acetate. This solution was stirred under a dry nitrogen atmosphere for 30 minutes at room temperature. 5 equivalents of boron trifluoride etherate were added with stirring at room temperature. The resulting solution was heated to 50 °C for a further 30 minutes. Dry sodium carbonate (10 g) was added slowly over 15 minutes. The resulting solution was stirred at 50 °C for a further 15 minutes. The product was precipitated from solution with the addition of 900 mL of dry and degassed methanol. A red/orange precipitate (CoBF) was obtained. The product was filtered under dry nitrogen and the obtained precipitate was washed three times with ice-cold methanol (50 mL). All washings were cooled and stored to recrystallise any lost product. The washed product was obtained as a dark orange/brown powder. This product was washed three times with hot water

(50 mL. The product was then vacuum dried for 48 hours to dryness to yield an orange/brown powder (CoBF).

9.3.4.2 Evaluation of the chain transfer co-efficient of CoBF with MMA

The chain transfer co-efficient, Cs of CoBF with MMA was evaluated by carrying out a series of bulk polymerisation reactions with various concentrations of MMA and initiator (AIBN). MMA was purified by passing through a column of activated basic alumina and stored under nitrogen prior to use. 4 mL of a stock solution containing 150 mg AIBN in 24 mL of MMA was measured into each of five ampoules along with between 0 and 0.4 mL of a stock solution containing 3.9×10^{-5} g mL^{-1} of CoBF in MMA. MMA was added appropriately to each reaction to give a total volume in each ampoule of 5 mL. These solutions were degassed by repeated freeze/pump/thaw cycles (x3) and sealed under a dry nitrogen atmosphere. Each reaction was heated to 60 °C for 15 minutes, after which time the reaction was cooled to 0 °C in an ice bath to terminate polymerisation and opened to air [6].

9.3.4.3 Evaluation of the chain transfer co-efficient of CoBF with DMAEMA

The chain transfer co-efficient, Cs of CoBF with DMAEMA was evaluated by carrying out a series of bulk polymerisation reactions with various concentrations of DMAEMA and initiator (AIBN). DMAEMA was purified by passing through a column of activated basic alumina and stored under nitrogen prior to use. 4 mL of a stock solution containing 150 mg AIBN in 24 mL of DMAEMA was measured into each of five ampoules along with between 0 and 0.4 mL of a stock solution containing 2.5×10^{-5} mg mL^{-1} of CoBF in DMAEMA. DMAEMA was added appropriately to each reaction to give a total volume in each ampoule of 5 mL. These solutions were degassed by repeated freeze/pump/thaw cycles (x3) and sealed under a dry nitrogen atmosphere. Each

reaction was heated to 60 °C for 15 minutes, after which time the reaction was cooled to 0 °C in an ice bath to terminate polymerisation and opened to air.

9.3.4.4 Preparation of PDMAEMA macromonomers from CCT mediated bulk polymerisation

Initiator (AIBN) and CoBF were accurately weighed into a Schlenk reaction tube. The Schlenk was sealed and purged with dry nitrogen. Monomer was added to the Schlenk and then the reaction solution was warmed to 70 °C for 46 hours. Reactions were terminated by cooling to 0 °C in an ice bath and by opening to air.

9.3.4.5 Aqueous solution CCT mediated polymerisation of methacrylic acid (MAA)

A series of experiments were performed containing different concentrations of transfer agent (CoBF) with respect to MAA where the concentration of transfer agent was varied between 5 and 122 ppm with respect to monomer. A batch component of the reaction mixture comprising free-radical initiator, water and chain-transfer agent (CoBF) was accurately added to a Schlenk reaction tube. A feed solution was prepared that contained MAA and additional transfer agent. The batch polymerisation mixture was heated to the reaction temperature of 55 °C. When the mixture had reached this temperature then the MAA was fed into the reaction over a period of 1 hour. For all of the reactions performed the amount of catalyst that was present in the batch component was double that which was present in the feed. The water-soluble free-radical initiator used in all cases was 2,2'azobis(N,N'dimethyleneisobutyramidine) dihydrochloride (ADMIBA.2HCl) and was added to give 0.4 weight % of initiator with respect to MAA. The reaction composition after the addition of monomer for all reactions contained 30 weight % solids. All reactions were terminated after 2 hours by cooling to 0 °C and opening to air.

9.3.4.6 Aqueous solution CCT mediated polymerisation of 2-(dimethylamino)ethyl methacrylate, hydrochloride salt (DMAEMA.HCl)

A series of experiments were performed containing different concentrations of transfer agent (CoBF) with respect to DMAEMA.HCl where the concentration of transfer agent was varied between 0 and 122 ppm with respect to monomer. A batch component of the reaction mixture comprising free-radical initiator, water and chain-transfer agent (CoBF) was accurately prepared into a Schlenk reaction tube. A feed solution was prepared that contained DMAEMA.HCl, water and additional transfer agent buffered with HCl to give pH 7, pH 5 and pH 3.5 feed solutions. The batch polymerisation mixture was heated to the reaction temperature of 55 °C. When the mixture had reached this0 temperature the DMAEMA was fed into the reaction over a period of 1 hour. The amount of catalyst that was present in the batch component was double that which was present in the feed and the water was distributed so that the feed:batch weight distribution was 35:10. The water-soluble free-radical initiator used in all cases was ADMIBA.2HCl and was added to give 0.19 weight % of initiator with respect to DMAEMA. The reaction composition after the addition of monomer for all reactions contained 12 weight % solids. All reactions were terminated after 24 hours by cooling to 0 °C and opening to air.

9.3.5 Preparation of 2-(dimethylamino)ethyl isobutyrate (DMAIEB)

Hydrogenation of DMAEMA was performed following the experimental procedure given by van der Wetering *et al*. DMAEMA (10 ml, 61 mmol) in CH_2Cl_2 (50 ml) was added to 50 mg of 10 % palladium on carbon (Pd/C). Hydrogenation was carried out for 12 hours in a stirred Parr reaction bomb at 60 PSi of hydrogen, and at ambient temperature. Pd/C was removed by filtration over celite and CH_2Cl_2 was evaporated under reduced pressure. Analysis by ^1H NMR gave excellent agreement with reported data with a yield 99.8 % [7].

9.3.6 Co-polymerisation of PDMAEMA macromonomers from CCTP with different acrylic monomers

9.3.6.1 Co-polymerisation of PDMAEMA macromonomer with Benzyl Methacrylate (BzMA) and Benzyl Acrylate (BzA)

A variety of different co-polymerisation reactions were performed where the ratio of [PDMAEMA]/[Monomer] was varied between 6 $x10^{-3}$ and 121 $x10^{-3}$. PDMAEMA macromonomer and initiator (AIBN) were weighed accurately into a Schlenk reaction tube. For all reactions 0.5 weight % of initiator (AIBN) was added with respect to monomer in the system. The Schlenk tube was vacuum filled with a dry nitrogen atmosphere. Monomer and toluene were added to the Schlenk tube to a solution containing 10 weight % solids. The reaction was stirred at 70 °C for 14 hours and was then terminated by cooling to 0 °C in an ice bath and by opening to air. The toluene was removed by evaporating under reduced pressure to obtain the product polymer.

9.3.6.2 Co-polymerisation of PDMAEMA macromonomer with Methacrylic Acid (MAA) and Acrylic Acid [AA]

A variety of different co-polymerisation reactions were performed where the ratio of [PDMAEMA]/[Monomer] was varied between 54 $x10^{-3}$ and 498 $x10^{-3}$. PDMAEMA macromonomer and initiator (CVA) were weighed accurately into a Schlenk reaction tube. For all reactions 1 weight % of initiator (CVA) was added with respect to total co-monomer in the system. The Schlenk tube was vacuum filled with a dry nitrogen atmosphere. Monomer and water were added to the Schlenk tube to a solution containing 25 weight % solids. The reaction was stirred at 70 °C for 2 hours and was then terminated by cooling to 0 °C in an ice bath and by opening to air. The product polymer was observed as a viscous gel. Concentrated potassium hydroxide solution was added to the polymerisation mixture until a homogeneous solution was obtained. The

solutions were precipitated into an excess of cold THF and the polymer was recovered by filtration.

9.3.7 Atom Transfer Mediated Polymerisation

9.3.7.1 Preparation of N-(n-pentyl)-2-pyridylmethanimine

An excess of n-pentylamine (29.0 mL, 0.25 mol) was added dropwise to pyridine-2-carboxaldehyde (20 mL, 0.21 mol) over activated molecular sieves cooled in an ice bath. After complete addition of amine the reaction was stirred at 25 °C for 2 hours. The product was purified by reduced pressure distillation to give a golden yellow oil. Analysis by ^{1}H NMR gave excellent agreement with reported data with a yield 97.1% [8].

9.3.7.2 Purification of Copper (I) Bromide

Copper (I) bromide was purified following the method of Keller and Wycoff [9]. Cu(I)Br (20 g) was ground in a pestle and mortar and then sulphuric Acid (0.5 M, 5 mL) was added to make a paste. The paste was added to sulphuric acid (0.1 M, 500 mL) and was stirred. The solid was allowed to settle and the excess acid was decanted. The remaining suspension was subsequently vacuum filtered and washed ensuring that the solid remained covered throughout. The product was then washed with glacial acetic acid (4 x 50 mL), methanol (3 x 50 mL) and diethyl ether (6 x 15 mL) . The product was dried under suction for 30 seconds and then dried in a vacuum oven at 75 °C for 25 minutes.

9.3.7.3 Typical homopolymerisation and statistical co-polymerisation procedure for Atom Transfer Polymerisation

Purified Cu(I)Br was accurately weighed into a Schlenk reaction tube and then the tube was sealed and purged with dry nitrogen. Monomer, solvent and ligand were all added at 25 °C. The solution was degassed by repeated

freeze/pump/thawing cycles (x3) and purged with dry nitrogen. The reaction mixture was then heated to the reaction temperature. When the contents had reached this temperature initiator was added via a degassed syringe. The polymerisation was sampled at suitable time periods throughout the reaction. The reaction was terminated by cooling to 0 °C in an ice bath and by opening to air. Catalyst residues were removed by filtering through a column of activated basic alumina. PMMA and PBzMA samples were isolated by precipitation into ice-cold hexanes. Different solvent, monomer and initiator systems were all examined. The respective reaction conditions are given in detail in chapter 5.

9.3.7.4 Block co-polymerisation procedure for Atom-Transfer Polymerisation

The initial block was prepared following a preparation using the protocol outlined in Section 9.3.7.3. Polymerisation was ideally terminated at 80 % monomer conversion. Polymer was purified by passing through a column of activated basic alumina. Each polymer was then distilled under reduced pressure to remove residual monomer. This polymer was then subsequently used as a macroinitiator species for Atom Transfer Polymerisation reaction with a second monomer species.

Purified Cu(I)Br and macroinitiator were accurately weighed into a Schlenk reaction tube and then the tube was sealed and purged with dry nitrogen. Monomer, solvent and ligand were all added at 25 °C. The solution was degassed by repeated freeze/pump/thawing cycles (x3) and purged with dry nitrogen. The Schlenk was then heated to reaction temperature. The polymerisation was sampled at suitable time periods throughout the reaction. The reaction was allowed to polymerise beyond the theoretical 100 % conversion point based on kinetics of the equivalent homopolymerisation of the monomer by ATP. Catalyst residues were removed by filtering through a column of activated basic alumina. Solvent was removed by reduced pressure evaporation.

9.3.7.5 Gradient co-polymerisation procedure for Atom-Transfer Polymerisation of PDMAEMA with PDEAEMA

Purified Cu(I)Br was accurately weighed into a Schlenk tube prior to the tube being sealed and purged with dry nitrogen. DMAEMA, solvent and ligand were all added at 25 °C. The solution was degassed by repeated freeze/pump/thawing cycles (x3) and purged with dry nitrogen. The reaction mixture was then heated to reaction temperature. When the contents had reached reaction temperature then initiator was added via a degassed syringe. The polymerisation was sampled at suitable time periods throughout the reaction. At 80 % monomer conversion DEAEMA was added to the reaction mixture via syringe and transfer and polymerisation was allowed to continue until complete monomer conversion was obtained. The reaction was terminated by cooling to 0 °C in an ice bath and by opening to air. Catalyst residues were removed by filtering through a column of activated basic alumina. Solvent was removed by reduced pressure evaporation.

9.3.8 Selective quaternisation of PDMAEMA-gradient-PDAEMA co-polymers

Quaternisation of PDMAEMA-gradient-PDEAEMA co-polymers species was performed with methyl iodide. PDMAEMA-gradient-PDEAEMA was dissolved to give a 10 weight % solution in THF in a round bottom flask. Alkyl halide was added accurately to each solution to give the desired degree of quaternisation based on the relative concentration of DMAEMA residues in the gradient co-polymer and the reaction was stirred at 25 °C for 24 hours. The quaternised product was recovered by evaporation of solvent at reduced pressure.

9.3.9 Reversible Addition-Fragmentation Transfer (RAFT) Polymerisation

9.3.9.1 Preparation of 2-phenylprop-2-yl dithiobenzoate

The transfer agent 2-phenylprop-2-yl dithiobenzoate was prepared from dithiobenzoic acid following the method of Le *et al* [10].

Dithiobenzoic acid was prepared following the method of Becke and Hagen [11]. Methanol (630 mL), sulfur (64.1 g, 2 mol), and 25 weight % aqueous solution of sodium methoxide (360 g, 2 mol) were mixed and stirred together at room temperature. To this, benzyl chloride (126 g, 1 mol) was added dropwise over a period of 1 hour. The reaction was then heated with stirring to 65 °C for 12 hours. The mixture was cooled and the resulting precipitate was filtered off. The solvent was removed from the filtrate with reduced pressure evaporation to yield pungent smelling dark red oil. The oil was dispersed into water (500 mL). The oil was neutralised with the addition of concentrated 5 M sodium hydroxide solution (50 mL) to give a purple solution. Dichloromethane (100 mL) was added and the dithiobenzoic acid was extracted into the organic layer with the addition of concentrated HCl (20 mL). The organic layer was isolated using reduced pressure evaporation to a yield dark red oil. The aqueous extracts were discarded into waste toxic solvent. The oil product was dispersed into water (500 mL) and then extracted into dichloromethane and isolated following the previous procedure. The dithiobenzoic acid was obtained as a pungent dark red oil (138.5 g, 0.9 mol, 89.8 % yield.

A mixture of dithiobenzoic acid (10.59 g), α-methyl styrene (10 g) and carbon tetrachloride (40 mL) were combined and the mixture was heated at 70 °C for 4 hours. Solvent was removed by reduced pressure evaporation to give a crude oil which was purified by column chromatography (aluminium oxide, n-hexane eluent) to give 2-phenylprop-2-yl dithiobenzoate (6.8 g, 36.4 %) as a dark purple/red oil).

9.3.9.2 Typical procedure for Reversible Addition-Fragmentation transfer (RAFT) Polymerisation

A stock solution containing monomer (0.14 mol), AIBN (20 mg) and 2-phenylprop-2-yl dithiobenzoate (60.7 mg, 2.23×10^{-4} mol) was prepared in toluene (5 mL). 4 mL aliquots of this stock solution were transferred to ampoules. Each solution was degassed by repeated freeze/pump/thaw cycles (x3) and sealed. The ampoules were heated at 60 °C for up to 20 hours. Ampoules were opened at periodic times throughout the reaction to determine molecular weight evolution for the polymerisation.

9.4 QUALITATIVE DYE-BINDING STUDIES

A litre surfactant stock solution was prepared using demineralised water, linear alkyl sulphonate (1.6 g), ethoxylated non-ionic A7 (0.4 g), sodium tripolyphosphate (1.2 g) and sodium carbonate (0.4 g).

Polymer stock solutions were prepared to give 0.1105 g of polymer in 250 ml of demineralised water.

Dyed cloths were prepared by mixing two white non-bleached cotton cloths (10 cm^2) in a solution of direct red 80 dye in demineralised water for 40 minutes. The cloths were dried by tumble drying for 30 minutes.

9.4.1 Determination of the degree of dye transfer from a dyed cotton cloth to a white non-bleached cotton cloth under simulated laundering conditions

Demineralised water (450 ml) was added to the stainless steel beaker. 25 ml of surfactant stock was added and the solution was warmed to 40 °C. 25 ml of polymer stock (1.7 weight % with respect to cotton) was added and the resulting solution was allowed to equilibrate for ten minutes. The cotton cloths (0.65 g)

were added to the beaker and then the mixture was maintained at 40 °C and was stirred at 70 rpm for 30 minutes. After washing, the cloths were removed and aired to evaporate all water. After the initial washing cycle the cloths were dried and analysed for dye-transfer. Two more wash and dry cycles were then performed where no further polymer was added. The delta reflectance at 534 nm (λ max for direct red 80) was measured for each cotton cloth before and after each washing and drying cycle.

9.4.2 Determination of the degree of dye-transfer from a solution of dye onto a white non-bleached cotton cloth under simulated laundering conditions

For each test a 10 μM solution of Direct Red 80 dye was prepared into 100 ml of demineralised water containing 5 ml of surfactant stock solution. A white non-bleached cotton cloth (13cm^2) and the test polymer (0.0435 gl^{-1}, 1.7 weight % with respect to cotton) were then added and the mixture was agitated in a tergometer for 30 minutes at 40 °C. The delta reflectance at 534 nm (λ max for direct red 80) was measured for the cotton cloth before and after each washing and drying cycle.

9.5 QUANTITATIVE DYE-BINDING STUDIES

9.5.1 Beer-lambert plot for direct red 80 dye in deionised water

A series of dye stock solutions were prepared based on the value of dye content from the elemental analysis data given in chapter 7 Section 7.2.2.1. Direct red 80 dye (0.225 g) was dissolved into 1 litre of deionised water to give a stock solution (5 x10^{-5} M). A series of solutions were prepared from this stock solution by dilution with deionised water to give the following; 1 x10^{-7} M, 3 x10^{-7} M, 6 x10^{-7} M, 1 x10^{-6} M, 3 x10^{-6} M, 6 x10^{-6} M, 1 x10^{-5} M and 1.9 x 10^{-5}

M. The UV/Visible spectra of these dye solutions were performed and the λ-max at 534 nm was obtained.

9.5.2 Measurement of the time required for dye-binding equilibration to occur between cross-linked poly(N-vinyl pyrrolidone) and Direct Red 80 dye

A dye stock solution (~1.9 x 10^{-5} M) was prepared in deionised water and divided into 50 ml aliquots. To each, 0.5 g (10 g.L^{-1}) of cross-linked poly(N-vinyl pyrrolidone) was added. Each mixture was shaken for a specific length of time between 1 and 25 minutes before removal and separation by centrifugation at 5000 rpm for 15 minutes. The absorption at 534 nm was determined for each solution to allow the evaluation of the concentration of dye in solution.

9.5.3 Measurement of the stability of the polymer-dye adduct $[CL.D]_S$

A stock solution of Direct Red 80 (~1.9 x 10^{-5} M) was prepared into deionised water. A 50 ml aliquot was mixed with 0.5 g (10 g.L^{-1}) cross-linked poly(N-vinyl pyrrolidone). The mixture was agitated for 25 minutes and then the cross-linked polymer-dye adduct was isolated by centrifugation (5000 rpm for 60 minutes). The absorption at 534 nm of the supernatant solution was determined and then the isolated polymer-dye adduct was added to 50 ml of deionised water and shaken for 25 minutes and then isolated. This process was repeated 3 more times to establish how much dye was lost from the polymer-dye adduct during each repetition.

9.5.4 Determination of the dye-binding constant, K_S for a water-insoluble polymer in deionised water

A stock solution of dye was prepared with 1 litre of deionised water to give a total dye concentration in solution of ~1.9 x 10^{-5} mol.L^{-1}. Five 50 ml aliquots of dye stock solution were pipetted into conical flasks and to these a known amount of water-insoluble polymer was added to give a range of dye concentrations between 10 g.L^{-1} and 80 g.L^{-1}. The conical flasks were sealed with bungs, the suspensions were agitated for 25 minutes and then the supernatant solutions were isolated by centrifugation at 5000 rpm for 60 minutes and the λ-max at 534 nm were determined.

9.5.5 Determination of the dye-binding constant, K_P for a water-soluble polymer in deionised water

A stock solution of Direct Red 80 dye (~1.9 x 10^{-5} M) was accurately prepared into 1 litre of deionised water. The UV/Visible spectrum of this stock solution was determined between 400 and 650 nm.

Eight 50 ml aliquots of the direct red 80 stock solution were pipetted into 250 ml conical flasks. To each aliquot a known amount of water-soluble polymer was added to give a range of polymer concentrations (0-5 g.L^{-1}). The conical flasks were sealed with rubber bungs and the solutions were agitated for 25 minutes. The λ-max at 534 nm was determined for each solution. To the resulting solutions an accurately weighed sample of a water-insoluble cross-linked polymer of known K_S was added. The cross-linked polymer used in all cases was cross-linked poly(N-vinyl pyrrolidone) (PVP-CL) at 40 g.L^{-1}. The mixture was then agitated for a further 25 minutes and then the supernatant solution was isolated by centrifugation at 5000 rpm for 60 minutes and the λ-max at 534 nm was determined.

9.5.6 Determination of the dye-binding constant, K_S for a water-insoluble polymer in surfactant stock solution

Surfactant stock solution was prepared into 1 litre of demineralised water containing linear alkyl sulphonate (1.6 g), ethoxylated non-ionic A7 (0.4 g), sodium tripolyphosphate (1.2 g) and sodium carbonate (0.4 g). A stock solution of dye was prepared with 1 litre of surfactant stock solution to give a total dye concentration in solution of ~1.9×10^{-5} $mol.L^{-1}$. Five 50 ml aliquots of dye stock solution were pipetted into conical flasks and to these a known amount of water-insoluble polymer was added to give a range of dye concentrations between 10 $g.L^{-1}$ and 80 $g.L^{-1}$. The conical flasks were sealed with bungs and the suspensions were agitated for 25 minutes and then the supernatant solutions were isolated by centrifugation at 5000 rpm for 60 minutes and the λ-max values at 534 nm were determined.

9.5.7 Determination of the dye-binding constant, K_P for a water-soluble polymer in surfactant stock solution

Surfactant stock solution was prepared into 1 litre of demineralised water containing linear alkyl sulphonate (1.6 g), ethoxylated non-ionic A7 (0.4 g), sodium tripolyphosphate (1.2 g) and sodium carbonate (0.4 g). A stock solution of Direct Red 80 dye (~1.9×10^{-5} M) was accurately prepared into 1 litre of surfactant stock solution. The UV/Visible spectrum of this stock solution was determined between 400 and 650 nm.

Eight 50 ml aliquots of the direct red 80 stock solution were pipetted into 250 ml conical flasks. To each aliquot a known amount of water-soluble polymer was added to give a range of polymer concentrations (0-5 $g.L^{-1}$). The conical flasks were sealed with bungs and the solutions were agitated for 25 minutes. The λ-max at 534 nm was determined for each solution. To the resulting solutions an accurately weighed sample of a water-insoluble cross-linked polymer of known K_S was added. The cross-linked polymer used in all cases

was cross-linked poly(N-vinyl pyrrolidone) (PVP-CL) at 40 $g.L^{1}$. The mixture was then agitated for a further 25 minutes and then the supernatant solution was isolated by centrifugation at 5000 rpm for 60 minutes and the λ-max at 534 nm was determined.

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